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SOME COMPUTATIONAL METHODS FOR THE STUDY
OF DIATOMIC MOLECULES

by

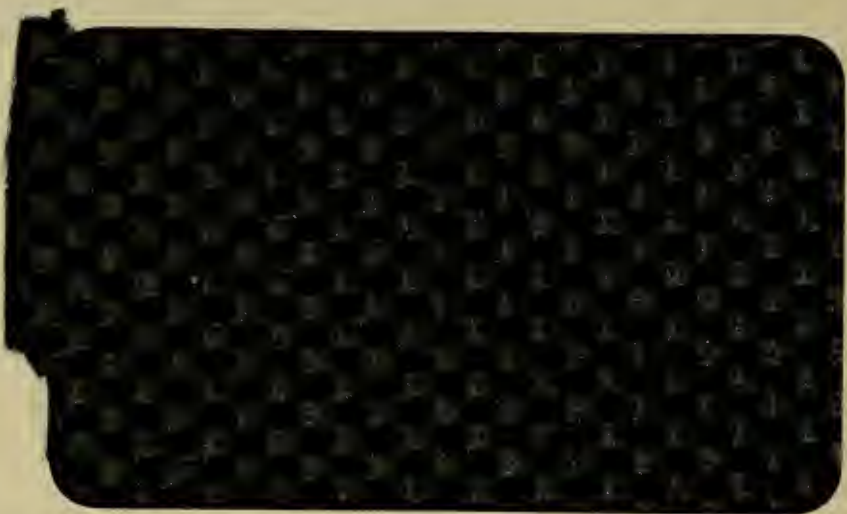
James W. Cooley

May 1, 1961

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ABSTRACT

A number of computational techniques are presented for the automatic machine calculation of the structure and properties of diatomic molecules. An automatic procedure is described which uses the Boolean operations of a binary computer for constructing N-electron pure state wave functions from a set of one-electron functions. Use of such automatic procedures permits one to calculate, by variational methods, electronic wave functions from a large number of electronic configurations and avoid the use and limitations of the self-consistent field procedure. The problem of minimizing a function of several variables was investigated and a search procedure which fits successive quadratic surfaces to calculated values was developed and programmed. The calculation of tables of molecular integrals of Slater-type orbitals, which have been published separately, is described. The numerical method for solving the radial Schrodinger

equation for bound states is described and an improved eigenvalue correction formula is derived. An analysis of the procedure and some practical means for improving its convergence and accuracy are also given. The technique was programmed as a computer subroutine and used for obtaining nuclear wave functions and expectation values of properties of some diatomic molecules. An LCAO calculation of an electronic wave function for H_2^+ , with a full optimization of the non-linear parameters by the minimization procedure mentioned above, was performed for the purpose of investigating the role of the orbital exponents and the applicability of the Virial Theorem, the Hellman-Feymann Theorem, and the static charge cloud model. The results lead to some suggestions which will be of use when applying similar methods to many-electron systems. The vibrational-rotational spectrum of H_2 , HD, and D_2 was calculated with two electronic wave functions reported by other workers and excellent agreement with experiment was obtained. A number of molecular constants which are required in the interpretation of radiofrequency spectra are also given.

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SOME COMPUTATIONAL METHODS FOR THE STUDY OF DIATOMIC MOLECULES

I INTRODUCTION

1. Purpose

Precise measurements of observable phenomena resulting from the internal structure of diatomic molecules can be obtained by spectroscopic methods. Accurate experimental techniques have been developed, over a long period of time, for obtaining absorption and emission spectra from the ultraviolet to the far infrared regions. The interpretation of such spectra by the application of quantum-mechanical principles, with simplifying assumptions, has led to well-established hypotheses concerning the particles involved and their configuration within the molecule. This has given a satisfactory theoretical explanation of chemical valence, an understanding of observed physical and chemical properties of gases, predictions of the existence and properties of molecules, and methods for detecting the presence of molecules and rare isotopic species, particularly in the planets, comets, and upper atmosphere.

More recently, the development, by N. Ramsey and others, of I. I. Rabi's [1] molecular beam magnetic and electric resonance methods has given extremely precise measurements in the low energy radiofrequency range where the spectrum is produced by relatively weak interactions between the nuclei, the surrounding electronic charge cloud, and external magnetic or electric fields.

In principle, at least, all of these observations can be predicted, *ab initio*, from hypotheses concerning the particles involved and the laws of quantum mechanics but the mathematical complexity of the equations for even the simplest molecular system makes their solution a formidable task.

The relatively recent development of automatic high-speed computers has made it possible to perform some of the extensive calculations involved and there is, as a result, an increasing need for the study, development, and application of appropriate computational methods. Among the problems for the numerical analyst, one finds many frequently-encountered computational problems such as the evaluation of rather complicated multi-dimensional definite integrals, matrix eigenvalue calculations, the integration of differential equations, and minimum value problems. In addition, there is a need and an opportunity to apply non-numerical procedures to the analysis of the

symmetry of molecules and the mathematical functions used to describe their structure. Such problems can be formulated and treated by techniques which use the ability of the electronic computer to perform logical operations.

The present work describes some computer-oriented techniques for the application of the laws of quantum mechanics to the problems of determining the basic structure of diatomic molecules. At times, calculations of the type described here yield results which can be compared directly with experiment to check the validity of the hypotheses and techniques used; they may predict the results of unobserved experimental phenomena; and, in many instances, they provide quantities which are necessary for the interpretation of experimental data but which cannot be directly measured.

-

2. The Born-Oppenheimer Approximation

A calculation of the wave functions of a molecule consisting of interacting electrons and nuclei is simplified by the use of the Born-Oppenheimer approximation [2] which consists in treating the motion of the electrons and the nuclei separately. Born and Oppenheimer have shown that the total molecular energy can be expanded in powers of $(m/M)^{1/2}$, where m is the electronic mass and M is an average nuclear mass, and that separating electronic and nuclear motions consists in neglecting high order terms in the small quantity $(m/M)^{1/2}$. From another point of view, the assumption is that the nuclei, being so heavy as compared with the electrons, move slowly enough for the electrons to adjust themselves instantaneously to each new nuclear configuration. This supports the further assumption that the change in electron configuration during nuclear motion is adiabatic: i.e., there is a negligible probability of a change from one electronic state to another during nuclear motion.

This separation of the various motions within the molecule separates the calculation of molecular structure into two parts: the calculation of the electronic wave functions as described in Chapter II, and the relatively

simple solution of the one-dimensional radial Schroedinger equation for which a numerical method is given in Chapter IV.

3. Weak Interactions

In addition to the Born-Oppenheimer approximation, one must make certain other simplifying assumptions to obtain equations which, first of all, actually determine a solution and, second, lead to practical means of calculating them. Accordingly, one assumes first that the nuclei and electrons are point masses and charges obeying the Coulomb law of force and that the magnetic moments of electron spin, nuclear spin, electron orbital motion, and molecular rotation do not interact. In addition, relativistic effects and interactions with an external environment are omitted.

These effects are small enough to allow one to get useful results with their omission and, when refinements are needed, to use first and second order perturbation methods as a means of evaluating the quantities omitted.

4. Atomic Units

Throughout the present work, all quantities will be expressed in atomic units [3] except where otherwise stated. The conversion factors used are:

$$\begin{aligned} 1 \text{ a.u.} &= 27.210 \text{ ev.} \\ " &= .435 \ 917 \times 10^{-10} \text{ erg} \\ " &= 219 \ 474.62 \text{ cm}^{-1} \\ " &= 6.579 \ 695 \times 10^9 \text{ Mc/sec.} \\ " &= .52917 \text{ \AA} \\ " &= 274.078 \text{ Bohr magnetons.} \end{aligned}$$

II THE ELECTRONIC WAVE EQUATION

1. Introduction

The Hamiltonian of the energy of the electrons of a diatomic molecule with the nuclei A and B at a fixed internuclear distance R, is, in atomic units,

$$(1.1) \quad \mathcal{H} = \sum_{i=1}^N H_i + \sum_{i=1}^{N-1} \sum_{j=i+1}^N r_{ij}^{-1}$$

where

$$H_i = -\frac{1}{2} \Delta_i - Z_a r_{ai}^{-1} - Z_b r_{bi}^{-1}.$$

Here, N is the number of electrons, Δ_i is the Laplacian operator for the i-th electron, Z_a and Z_b are the charges on nuclei A and B, r_{ai} and r_{bi} are the distances of the i-th electron from A and B, and r_{ij} is the distance between the i-th and j-th electrons.

A wave function for this system is an N-electron function $\underline{\Psi}(1,2,\dots,i,\dots,N)$, where i represents the three space coordinates x_i, y_i, z_i , and the spin coordinate ξ_i of the i-th electron. It is an eigenfunction of the differential equation

$$(1.2) \quad \mathcal{H} \underline{\Psi} = E \underline{\Psi}$$

for some eigenvalue E which is the energy of the system in the state $\underline{\Psi}$. In variational methods, approximate solutions of (1.2) are found by letting a trial wave function $\underline{\Psi}$ range over some necessarily limited set of functions and taking as the "best" solutions those for which the expectation value of the energy,

$$(1.3) \quad E = \int \underline{\Psi}^* \mathcal{H} \underline{\Psi} dV / \int \underline{\Psi}^* \underline{\Psi} dV ,$$

attains a minimum. Here, $\int dV$ denotes integration over all $3N$ space and N spin coordinates.

An important aspect of the computational problem is the selection of trial wave functions suitable for the problem and for the particular eigenfunction one wants to approximate.

2. Historical Survey

Hartree's procedure [4], in obtaining solutions of this type of problem for atoms was to form a simple product trial wave function

$$(2.1) \quad \underline{\Psi} = \psi_1(1) \psi_2(2) \dots \psi_N(N)$$

where

$$\psi_1 = \phi_1^\alpha, \quad \psi_2 = \phi_1^\beta, \quad \psi_3 = \phi_2^\alpha, \quad \psi_4 = \phi_2^\beta, \dots,$$

with α and β denoting the one-electron spin eigenfunctions. The space functions were, in spherical polar coordinates,

$$(2.2) \quad \phi_i = R_i(r) Y_{\ell_i, m_i}(\theta, \phi)$$

where the Y_{ℓ_i, m_i} 's are the complex spherical harmonics and the $R_i(r)$'s are numerical radial functions. By a somewhat heuristic argument, he determined the radial functions $R_i(r)$ by considering the Hamiltonian of the i -th electron in the potential field of all the others,

$$(2.3) \quad \mathcal{L}_i = -\frac{1}{2} \Delta_i - Z r_i^{-1} + \sum_{j \neq i} \int \psi_j^*(j) \psi_j^*(j) r_{ij}^{-1} dv_j$$

where Z is the nuclear charge and $\int dv_j$ denotes integration over the space and spin coordinates of electron j .

Slater pointed out [5] that a trial wave function should satisfy the Pauli exclusion principle and should be antisymmetric in the coordinates of the electrons. To accomplish this, he suggested the use of "Slater Determinants" (SD's),

$$\begin{aligned}
 \underline{\Psi} &= (N!)^{-1/2} \det \{ \psi_1(1), \dots, \psi_N(N) \} \\
 (2.4) \quad &= (N!)^{-1/2} \begin{vmatrix} \psi_1(1) & \dots & \psi_N(1) \\ \vdots & & \vdots \\ \psi_1(N) & \dots & \psi_N(N) \end{vmatrix} .
 \end{aligned}$$

Fock [6] then gave a rigorous derivation of the conditions under which the energy (1.3) attains a minimum when computed with the antisymmetrized product wave function (2.4). His result was that the one-electron functions which diagonalize the one-electron operator,

$$(2.5) \quad \mathcal{L}_i = -\frac{1}{2} \Delta_i - Z r_i^{-1} + \sum_{j=1}^N \int \psi_j^*(j) r_{ij}^{-1} (1 - P_{ij}) \psi_j(j) dv_j$$

will minimize (1.3). When \mathcal{L}_i operates on a one-electron function $\psi_i(i)$, the operator P_{ij} exchanges the coordinates of electrons i and j before the integration takes place. Thus, the use of the antisymmetrized trial wave functions introduces an "exchange term" in the one-electron operator.

Integrating over angular and spin coordinates gives integro-differential equations in the radial functions $R_i(r)$ corresponding to (2.3) or (2.5). The computational procedure consists in forming a first estimate of all

$R_1(r)$'s to obtain a one-electron effective potential for each electron. The resulting one-dimensional differential equation is then solved for a new set of $R_1(r)$. This process is repeated until the input $R_1(r)$'s are the same as the output. In general, the use of such an iterative procedure with a single-determinant wave function is known as the Hartree-Fock (HF) scheme or the "self-consistent field" (SCF) method.

The above methods are characterized by the fact that an N-electron wave function is constructed of one-electron functions. This is somewhat distinct from other rather successful methods in which the N-electron wave function is formed from functions of the coordinates of several electrons. An example is the treatment of the two-electron He-like systems by Hylleraas^{*}. Combinations of the two points of view, in which one-electron functions are combined with two-electron functions, have also been applied [8]. The great success of Hylleraas on two-electron systems tended to discourage somewhat the use of the one-electron approach but the lack of ready applicability of the Hylleraas-type treatment to many-electron systems contributed to a reviving interest in the

* For a brief summary and bibliography of Hylleraas' work, see Ref. [7].

latter. Of perhaps more importance in this revival is the refinement of mathematical and computational techniques and the availability of electronic computers capable of implementing them.

In going from atoms to molecules, the Heitler-London-Pauling-Slater or valence bond (VB) method [7] was applied with success in giving a quantum-mechanical picture of chemical valence. By this method, the N-electron molecular wave functions are constructed in a rather simple manner from the wave functions of the individual atoms in the molecule. An approach to the problem from another point of view is contained in the Hund-Mulliken or molecular orbital (MO) method, which assigns each electron to a one-electron molecular wave function in a determinantal molecular wave function. The latter has its advantages in describing processes of ionization and excitation. The line of development represented by the very successful James and Coolidge [9] treatment of the hydrogen molecule with a two-electron function falls in the same category here as the Hylleraas treatment does in the case of atoms.

The main extension of the Hartree-Fock SCF method to molecules is in the treatment given by Lennard-Jones [10, 11], Hall [12], Roothaan [13], and others. Here,

instead of treating numerical functions, a convenient set of analytic basis functions, χ_1, χ_2, \dots , of one-electron space coordinates is used to form MO's of the form

$$(2.6) \quad \phi_i = \sum_k \chi_k c_{k,i} .$$

Multiplying all MO's by α and β spin functions gives twice as many molecular spin orbitals (MSO's). These will be denoted by

$$(2.7) \quad \begin{aligned} \psi_i &= \phi_{\frac{1}{2}(i+1)} \alpha && \text{if } i \text{ is odd} \\ \psi_i &= \phi_{\frac{1}{2}i} \beta && \text{if } i \text{ is even .} \end{aligned}$$

By forming an N-electron SD wave function of the form (2.4) from the functions (2.7), the integro-differential equations of the SCF method are replaced by vector-matrix equations which determine the coefficients in (2.6). A large number of calculations of the ground states of closed-shell systems have been performed by these methods using, as basis functions, the hydrogenic-like atomic functions to be defined later.

However, the HF scheme is somewhat difficult or unsatisfactory when applied to open-shell systems [14, 15].

Furthermore, even in the latter applications, since the spin-paired MSO's are constrained in having the same space functions, the motions of the electrons occupying them are not correlated by the Coulomb repulsion between them. The energy of this constraint has come to be known as the "correlation energy" and has been calculated to amount to approximately 1.0 to 1.6 ev. per electron pair in He-like atoms [16]. Some procedures, such as the extended Hartree-Fock methods [17], have given some improvement in results.

Another difficulty in the use of the single-determinant trial wave function is that it is suitable only for certain eigenfunctions of the problem and not at all for others. This aspect will be discussed in greater detail below. The recent line of development which has given some improvement in energy values and properties is the use of configuration interaction (CI). This receives some mathematical encouragement from the fact that the set of SD's obtained by selecting N one-particle functions in all possible ways from a complete set of such functions is complete in the Hilbert space of all antisymmetric N -particle functions. This leads one to believe that if a finite set of one-particle functions is sufficiently adequate in describing the motions of the individual electrons in a system, then

a set of SD's formed from them should be able to represent the N-electron wave functions of the system. One rather successful procedure for doing this is to go through the SCF process to optimize a single-determinant wave function $\underline{\Psi}_0$ by determining the "best" MO's of the form (2.6). In diagonalizing the one-electron operator, one obtains extra solutions, or "virtual orbitals" which do not appear in the determinant. Then, the orbital energies, which appear as eigenvalues of the one-electron operator, may be used as criteria for replacing occupied MO's by virtual MO's in various ways. The set of SD's $\underline{\Psi}_1, \underline{\Psi}_2, \dots$, so formed, is then used in a wave function of the form

$$(2.8) \quad \underline{\Psi} = \sum_{K=0} \underline{C}_K \underline{\Psi}_K .$$

By the variation theorem, the optimal \underline{C}_K 's are given by the solutions of the secular equations

$$(2.9) \quad \sum_L (\underline{H}_{KL} - E \underline{S}_{KL}) \underline{C}_L = 0 , \quad K = 0, 1, 2, \dots ,$$

where

$$\begin{aligned} \underline{H}_{KL} &= \int \underline{\Psi}_K^* \mathcal{H} \underline{\Psi}_L^* dV \\ \underline{S}_{KL} &= \int \underline{\Psi}_K^* \underline{\Psi}_L^* dV . \end{aligned}$$

In this way, most of the solution is given by a single determinant and the mixing-in of the SD's containing virtual orbitals gives a small correction. In calculations for HF Karo and Allen [18] got a binding energy of 1.3699 ev. by the SCF procedure and raised this to 2.1166 ev. by using seven configurations. The experimental binding energy of HF is 6.08 ev. Kotani et al. [19] raised the computed binding energy of O_2 from .795 ev. to 3.629 ev. by using 15 configurations. Here, the experimental value is 5.08 ev.

The purpose of the present investigation is to study the possibility of directly forming trial wave functions of the form (2.8) from MO's which are not necessarily SCF MO's. By taking all possible determinants in linear combinations suitable for the particular eigenfunction desired, one does not impose the constraints leading to the correlation error and one can form good approximate wave functions for eigenfunctions other than the ground state.

3. Pure State Wave Functions

Considered as an operator on the Hilbert space of all acceptable wave functions, the Hamiltonian \mathcal{H} , defined by (1.1), is a Hermitian operator. Here, trial

wave functions for the variational procedure for calculating approximations to the eigenfunctions and eigenvalues of \mathcal{H} are constructed so that they are, for all values of the variational parameters, eigenfunctions of certain Hermitian operators which commute with \mathcal{H} and with each other. A wave function which is simultaneously an eigenfunction of all the commuting operators described below, but not necessarily of \mathcal{H} , will be called a "pure state wave function" and will be classified by giving the corresponding eigenvalues of the commuting operators. The properties of these operators imply that the eigenfunctions of \mathcal{H} corresponding to each eigenvalue E of \mathcal{H} are linear combinations of pure state wave functions. It will now be shown how the special properties of the pure state wave functions may be used to advantage in the computational procedure.

Suppose \mathcal{M} is one of the commuting operators and that λ and λ' are distinct eigenvalues of \mathcal{M} . Then, the corresponding eigenfunctions, Φ and Φ' , of \mathcal{M} , whether they be exact eigenfunctions of \mathcal{H} or simply variational trial wave functions, satisfy

$$(3.1) \quad \int \Phi^* \Phi' dV = 0 .$$

and

$$(3.2) \quad \int \bar{\Phi}^* \mathcal{M} \Phi' \, dV = 0 .$$

If a finite set of eigenfunctions, $\bar{\Phi}_1, \bar{\Phi}_2, \dots, \bar{\Phi}_M$ of \mathcal{M} is then chosen and a trial wave function is expressed in the form

$$(3.3) \quad \bar{\Phi} = \sum_K c_K \bar{\Phi}_K ,$$

the optimal coefficients of (3.3) satisfy

$$(3.4) \quad \sum_L (H_{KL} - S_{KL} E) c_L = 0$$

where

$$(3.5) \quad H_{KL} = \int \bar{\Phi}_K^* \mathcal{M} \bar{\Phi}_L \, dV$$

$$(3.6) \quad S_{KL} = \int \bar{\Phi}_K^* \bar{\Phi}_L \, dV .$$

From (3.1) and (3.2), it is seen that the $\bar{\Phi}_K$'s can be ordered so that the matrix of coefficients of the c_L 's in (3.4) appears as a block diagonal matrix with each block corresponding to a distinct eigenvalue of \mathcal{M} . Thus, each eigenfunction is obtained as an eigenvector of a particular block matrix with the sum in (3.3) going over only eigenfunctions of \mathcal{M} having the eigenvalue

corresponding to the block in question. In this way, an approximation to the exact eigenfunction for the selected value of λ is found by solving a relatively small matrix equation. Some further advantages are that: the degeneracies in \mathcal{N} associated with \mathcal{M} result in blocks on the diagonal which are identical so that, in effect, a number of different λ -state solutions may be obtained in a single process; non-linear parameters in the trial wave functions may be varied without destroying the properties (3.1) and (3.2); and the variation theorem implies that the energies obtained are upper bounds of the exact energies for the particular λ -state under consideration.

We will now consider specific operators which commute with \mathcal{N} . Denoting the molecular axis by z , the z -component of total angular momentum is

$$(3.7) \quad \mathcal{L}_z = \sum_{i=1}^N l_{zi}$$

where $l_{zi} = -\sqrt{-1} \partial/\partial\phi_i$ is the operator corresponding to the z -component of angular momentum of the i -th electron. Eigenfunctions $\Phi(L_z)$ of \mathcal{L}_z corresponding to the eigenvalues $L_z = 0, \pm 1, \pm 2, \dots$, will be denoted by

$$(3.8) \quad \Sigma, \Pi^+, \Delta^+, \dots,$$

respectively, in spectroscopic notation. Following international nomenclature, we let

$$(3.9) \quad \Lambda = |L_z| .$$

The second operator to be considered is σ_v , the reflection of the wave function in a plane containing the molecular axis. It can easily be shown from the symmetry of the molecule that the dependence of $\underline{\psi}(L_z)$ on ϕ_i , $i = 1, 2, \dots, N$ is such that

$$(3.10) \quad \sigma_v \underline{\psi}(L_z) = \underline{\psi}^*(L_z) = \underline{\psi}(-L_z) .$$

Therefore, when $\Lambda \neq 0$, only the eigenfunctions $\underline{\psi}(\Lambda)$ (i.e. with $L_z > 0$) need be found since, if needed, $\underline{\psi}(-\Lambda)$ may be formed by simply operating with σ_v . It should be noted here that some workers use the " \pm " in the notation of (3.8) to denote the two eigenfunctions

$$(3.11) \quad \underline{\Phi}^{\pm}(\Lambda) = \underline{\psi}(\Lambda) \pm \underline{\psi}^*(\Lambda)$$

of σ_v . From (3.10) and (3.11) it is seen that the eigenvalues of σ_v are ± 1 and that the eigenfunctions of σ_v are the real and imaginary parts of the eigenfunctions (3.8) of \hat{L}_z . The Σ -type functions are

doubly degenerate eigenfunctions of \mathcal{L}_z and, in this case, the eigenfunctions (3.11) of σ_v , with $\Lambda = 0$, will be constructed and denoted by Σ^\pm .

In the special case of a homopolar diatomic molecule (having nuclei with equal charges), another operator resulting from the symmetry of the molecule is \hat{i} , the inversion of the molecule through its center. This can do no more than change the sign of the wave function, so its eigenvalues are ± 1 . The corresponding eigenfunctions are referred to as "gerade" and "ungerade" functions, respectively, and are given the subscripts g and u .

Finally, the total spin operator is defined by

$$(3.12) \quad \mathcal{S} = \sum_{i=1}^N \mathcal{S}_i$$

where \mathcal{S}_i is the spin operator for the i -th electron. Since \mathcal{H} and the operators considered above are independent of electron spin, they commute with both \mathcal{S}^2 and the component $\mathcal{S}_{z'}$, of \mathcal{S} along any axis z' . The eigenvalues of \mathcal{S}^2 are $s(s+1)$, where

$$(3.13) \quad \begin{aligned} s &= 0, 1, \dots, N/2 && \text{if } N \text{ is even} \\ s &= 1/2, 3/2, \dots, N/2 && \text{if } N \text{ is odd,} \end{aligned}$$

and are of degeneracy $2s+1$. This degeneracy is removed by $\mathcal{S}_{z'}$, which has the eigenvalues

$$(3.14) \quad s_{z'} = -s, -s+1, \dots, s-1, s \quad .$$

If $\Lambda \neq 0$, one usually considers electronic wave functions whose electron spin is coupled to the angular momentum \mathcal{L}_z . In this case, the z' -axis is taken as the molecular axis, z , and s_z is denoted, in the standard notation of the literature, by Σ (the quantum number Σ is not to be confused with the Σ eigenfunction in (3.8)). Therefore, the prime will be dropped from $\mathcal{S}_{z'}$, but one is to keep in mind that the spin axis is arbitrary and other coupling schemes may be considered.

In the next four sections, automatic procedures for generating variational trial electronic wave functions which are eigenfunctions of the operators \mathcal{L}_z , σ_v (if $\Lambda = 0$), i (if the molecule is homopolar), \mathcal{S}^2 , and \mathcal{S}_z will be described.

4. Construction of the Slater Determinants

The most extensively-used basis functions for constructing the MO's (2.6) are the atomic orbital (AO) functions first suggested by Slater for atomic calculations. These are of the form

$$(4.1) \quad (n, \ell, m) = (2\mu)^{n+\frac{1}{2}} [(2n)!]^{-\frac{1}{2}} r^{n-1} e^{-\mu r} Y_{\ell m}(\theta, \phi)$$

and are referred to as Slater orbitals (SO's) or Slater-type orbitals (STO's), depending upon whether or not the μ 's are given the values recommended by Slater for use with atoms. In particular, the STO's used in the calculations reported here are, in spectroscopic notation,

$$(4.2) \quad \begin{aligned} 1s &= \mu^{3/2} \pi^{-1/2} e^{-\mu r} \\ 2s &= \mu^{5/2} (3\pi)^{-1/2} e^{-\mu r} \\ 2p\sigma &= \mu^{5/2} \pi^{-1/2} e^{-\mu r} \cos \theta \\ 2p\pi^{\pm} &= \mu^{5/2} (2\pi)^{-1/2} e^{-\mu r} \sin \theta e^{\pm i\phi} . \end{aligned}$$

These five functions are put on each nucleus with the polar axis pointing toward the other nucleus. This gives a total of ten basis functions χ_1, \dots, χ_{10} which are, by the manner in which they are defined, eigenfunctions of ℓ_z . To make the MO's orthonormal, the overlap matrix \underline{S} , whose elements are

$$(4.3) \quad S_{ij} = \int \chi_i^* \chi_j d\tau ,$$

with $\int d\tau$ denoting integration over the one-electron space coordinates, is diagonalized by the Jacobi

iteration-rotation method [20]. This gives an orthonormal matrix \underline{U} such that

$$(4.4) \quad \underline{U}^\dagger \underline{S} \underline{U} = \underline{D}$$

is diagonal. Then the matrix

$$(4.5) \quad \underline{T} = \underline{U} \underline{D}^{-\frac{1}{2}}$$

gives a transformation to a set of MO's expressed as linear combinations of atomic orbitals (LCAO),

$$(4.6) \quad \phi_j = \sum_{i=1}^{10} \chi_i t_{ij}, \quad j = 1, 2, \dots, 10,$$

which satisfy the orthonormality condition

$$(4.7) \quad \int \phi_i^* \phi_j d\tau = \delta_{ij}.$$

If the molecule is homopolar, the orthonormalization procedure can be made to yield eigenfunctions of the operator \hat{L} . Due to the symmetry of the AO's, the MO's so constructed are also eigenfunctions of \hat{L}_z . Letting σ and π^\pm denote the MO's with $l_z = 0$ and ± 1 , respectively, the MO's $\phi_1, \phi_2, \dots, \phi_{10}$ will be labelled

$$(4.8) \quad 1\sigma_g, 1\sigma_u, 2\sigma_g, 2\sigma_u, 3\sigma_g, 3\sigma_u, \pi_g^-, \pi_u^-, \pi_g^+, \pi_u^+$$

in the usual spectroscopic notation. When a calculation is completed, the numbers 1, 2, and 3 on the resulting σ -type MO's are generally assigned in the order of the energies associated with them, starting at the lowest. To simplify notation, the symbols in (4.8) will be used here whether or not the molecule is homopolar. It is also to be understood that in the latter case, operations having to do with the operator \hat{I} are omitted.

Multiplying these ten MO's by α and β spin functions gives a total of twenty MSO's, $\psi_1, \psi_2, \dots, \psi_{20}$, which are indexed as in (2.7). With a basis for a one-electron function space thus established, a basis for an N-electron function space is taken as the set of $\binom{20}{N}$ SD's,

$$(4.9) \quad \underline{\Psi}_K = (N!)^{-\frac{1}{2}} \det \{ \psi_{k_1}(1), \dots, \psi_{k_N}(N) \} ,$$

obtained by selecting k_1, k_2, \dots, k_N in all possible ways from among the integers 1, 2, ..., 20. To avoid redundancy, the sets (k_1, k_2, \dots, k_N) will be ordered $k_1 < k_2 < \dots < k_N$. In the notation, K will denote such an ordered set but, when convenient, K will be treated as an index ($= 1, 2, \dots$) going over all ordered sets. As a result of the orthonormality of the MSO's, $\psi_1, \psi_2, \dots, \psi_{20}$, the SD's (4.9) satisfy the orthonormality condition

$$(4.10) \quad \int \underline{\psi}_K^* \underline{\psi}_L \, dV = \delta_{KL} ,$$

where $\delta_{KL} = 1$ if the ordered sets K and L are the same and $\delta_{KL} = 0$ if they are not. In addition, the SD's are already eigenfunctions of \mathcal{S}_z , \mathcal{L}_z , and \hat{i} whose eigenvalues can easily be computed. A procedure for forming linear combinations of the SD's which are also eigenfunctions of \mathcal{S}^2 and σ_v will be given in the next three sections.

In the Hartree-Fock SCF method for closed or open shells, one, in effect, calculates a unitary transformation \underline{R} of the \underline{T} matrix (4.5),

$$(4.11) \quad \underline{T}^{\text{SCF}} = \underline{T} \underline{R} ,$$

giving a set of MO's

$$(4.12) \quad \phi_j^{\text{SCF}} = \sum_i \chi_i t_{ij}^{\text{SCF}}$$

such that the energy, E^{SCF} , for a single SD $\underline{\psi}^{\text{SCF}}$ constructed of the MO's (4.12), attains a minimum. Since the wave function $\underline{\psi}^{\text{SCF}}$ can be expressed as a linear combination of the basis set $\underline{\psi}_K$, $K = 1, 2, \dots$, described above, the wave function obtained by simply finding the best linear combination of the $\underline{\psi}_K$'s will be better than $\underline{\psi}^{\text{SCF}}$. On the other hand, if the computational effort

involved with such a large number of SD's is too formidable, or if SCF MO's are already available, it may be practical to use the SCF MO's (4.12) instead of the MO's (4.6) and restrict the set of SD's to those which contain the MO's having the lowest eigenvalues (orbital energies) of the one-electron operator of the SCF scheme. In this case, the automatic procedures described here for constructing pure state functions permit the use of far more SD's than one could otherwise include.

In the following methods for constructing pure state wave functions, the only properties of the MO's considered are, of course, their symmetry in the molecule. The author would like to suggest that the use of some other set of functions having the correct molecular symmetry would probably be better. As an example, MO's of the form

$$(4.13) \quad f(\xi, \eta) \exp (-\mu\xi + im\phi)$$

where

$$\xi = (r_a + r_b)/R, \quad \eta = (r_a - r_b)/R$$

not only seem more appropriate, but give wave functions quite like the ones used by James and Coolidge [9] and others except that the present functions would not explicitly contain the distance between pairs of electrons.

A particularly convenient set of functions of the form (4.13) is the set of solutions of H_2^+ . Such a choice of basic MO's would also avoid the problem of "over-completeness" which results from the fact that the STO's form a complete set on each center. The effect of the overcompleteness is that, with a large number of STO's on both centers, any function on one center is almost a linear combination of those on the other and, as a consequence, there is a large indeterminacy in the SD's which becomes more serious as R , the internuclear distance, decreases.

5. The Projection Operator Technique

The use of projection operators by the methods developed by Löwdin [21, 22] not only is conceptually simple but also leads to systematic procedures which are well-suited for automatic machine methods. A general description of the fundamental ideas and the derivation of some necessary formulas are given in this section.

Suppose that $\bar{\Phi}$ is an arbitrary function and that \mathcal{M} is a Hermitian operator for some function space containing $\bar{\Phi}$. Under certain conditions, it is possible to express $\bar{\Phi}$ in the form

$$(5.1) \quad \bar{\Phi} = \sum_k c_k \bar{\Phi}_k$$

where $\overline{\Phi}_1, \overline{\Phi}_2, \dots$ are eigenfunctions of \mathcal{M} corresponding to distinct eigenvalues $\lambda_1, \lambda_2, \dots$. When this is so, the projection operator

$$(5.2) \quad \mathcal{O}_k = \prod_{k' \neq k} (\lambda_{k'} - \mathcal{M}) / (\lambda_{k'} - \lambda_k) ,$$

when applied to $\overline{\Phi}$, yields

$$(5.3) \quad \mathcal{O}_k \overline{\Phi} = c_k \overline{\Phi}_k .$$

Thus, an eigenfunction of \mathcal{M} is formed whose eigenvalue is the pre-selected λ_k . The denominator in (5.2) gives \mathcal{O} (we drop the subscript k for the rest of the discussion) the property

$$(5.4) \quad \mathcal{O}^2 = \mathcal{O} .$$

Suppose, for the moment, that one has a set of orthonormal functions $\overline{\Psi}_1, \overline{\Psi}_2, \dots$ such that for every $\overline{\Psi}_K$ in the set, $\mathcal{M}\overline{\Psi}_K$ is a linear combination of functions in the set. Then, if \mathcal{O} is as defined in (5.2) one can write

$$(5.5) \quad \mathcal{O}_L = \mathcal{O}\overline{\Psi}_L = \sum_K \overline{\Psi}_K c_{KL}$$

for some set of coefficients c_{KL} . The elements of the overlap matrix of the projections \mathcal{O}_L are

$$\begin{aligned}
 \int \mathfrak{H}_K^* \mathfrak{H}_L \, dV &= \int (\mathcal{O}\underline{\Psi}_K)^* (\mathcal{O}\underline{\Psi}_L) \, dV \\
 &= \int \underline{\Psi}_K^* \mathcal{O} \underline{\Psi}_L \, dV = \sum_{L'} c_{L'L} \int \underline{\Psi}_K^* \underline{\Psi}_{L'} \, dV \\
 (5.6) \qquad &= c_{KL} .
 \end{aligned}$$

The quantum-mechanical "turnover rule" is valid here since \mathcal{O} is Hermitian. Since the c_{KL} 's are the elements of the overlap matrix of the \mathfrak{H}_K 's, the Schmidt orthogonalization procedure can be applied to the \mathfrak{H}_K 's by simply triangularizing the matrix of c_{KL} 's by fundamental row operations. This process discards the dependent \mathfrak{H}_K 's and yields a new set of \mathfrak{H}_K 's and c_{KL} 's having the property (5.6). Hence the formula

$$\begin{aligned}
 c_{KK} &= \int \mathfrak{H}_K^* \mathfrak{H}_K \, dV = \sum_{L', L''} c_{L'K} c_{L''K} \int \underline{\Psi}_{L'} \underline{\Psi}_{L''} \, dV \\
 (5.7) \qquad &= \sum_L c_{LK}^2
 \end{aligned}$$

for the normalization factor is valid both before and after orthogonalization. This is not only useful as a check during the calculation but also enables the program to test for a zero \mathfrak{H}_L during the orthogonalization by simply testing the L -th diagonal element of the c_{KL} matrix.

It will be convenient, at this point, to introduce vector and matrix notation. A set of functions will be written as a row vector and the coefficients of a linear combination of functions will be written as a column vector. For some matrices, a symbolic subscript will be used to denote which basis is used to define the elements. Accordingly, (5.5) and (5.6) can be written

$$(5.8) \quad \underline{\Psi} = \mathcal{O} \underline{\psi} = \underline{\psi} \underline{C}$$

$$\int \underline{\Psi}^\dagger \underline{\Psi} dV = \underline{C}.$$

Here, " \dagger " denotes the conjugate transpose and $\int dV$ indicates that the integration is over the entire space on which the functions are defined.

In this notation,

$$\begin{aligned} \underline{H}_{\underline{\Psi}} &= \int \underline{\Psi}^\dagger \mathcal{H} \underline{\Psi} dV = \int (\mathcal{O} \underline{\psi})^\dagger \mathcal{H} \mathcal{O} \underline{\psi} dV \\ &= \int \underline{\psi}^\dagger \mathcal{H} \mathcal{O} \underline{\psi} dV = \int \underline{\psi}^\dagger \mathcal{H} \underline{\psi} dV \underline{C}, \end{aligned}$$

where the properties that \mathcal{O} is Hermitian, commutes with \mathcal{H} , and satisfies (5.4) have been used. Hence, the equation

$$(5.9) \quad \underline{H}_{(\mathcal{N})} = \underline{H} \underline{\Psi} \underline{C}$$

gives the relation between the two matrix representations of \mathcal{N} . Equation (5.9) is valid if \mathcal{N} is replaced by any operator which commutes with \mathcal{M} .

The Schmidt orthogonalization procedure, followed by division by the normalization constant $\sqrt{c_{KK}}$, yields a transformation to an orthonormal set of independent pure state functions

$$(5.10) \quad \underline{\Phi} = \underline{(\mathcal{N})} \underline{P} = \underline{\Psi} \underline{C} \underline{P} = \underline{\Psi} \underline{A}$$

where

$$\underline{A} = \underline{C} \underline{P}.$$

Since linearly dependent columns of \underline{C} are discarded, \underline{C} is a rectangular $n \times r$ matrix, where n is the number of $\underline{\Psi}_K$'s and r is the rank of \underline{C} . The matrix \underline{P} , which gives the transformation to orthonormal functions, is an $r \times r$ triangular matrix and \underline{A} is a matrix of the same dimensions as \underline{C} . From (5.9) and (5.10), one gets

$$\underline{H} \underline{\Phi} = \underline{P}^\dagger \underline{H}_{(\mathcal{N})} \underline{P} = \underline{P}^\dagger \underline{H} \underline{\Psi} \underline{C} \underline{P}.$$

Hence, the matrix of \mathcal{N} with respect to the pure state functions can be expressed in terms of the matrix of \mathcal{N} with respect to the basis $\underline{\Psi}$ by the relation

$$(5.11) \quad \underline{\underline{H}}_{\underline{\underline{\Phi}}} = \underline{\underline{P}} \underline{\underline{H}} \underline{\underline{\Psi}} \underline{\underline{A}} \quad .$$

The SD's of the previous section and the operators \mathcal{S}^2 and σ_v have the properties assumed here for the basis functions $\underline{\underline{\Psi}}_K$ and the operator \mathcal{M} . The elements of the matrix $\underline{\underline{H}}_{\underline{\underline{\Psi}}}$ can be expressed in terms of the integrals

$$\begin{pmatrix} k \\ \ell \end{pmatrix} = \int \psi_k^{*(1)} H_1 \psi_\ell^{(1)} dv_1$$

(5.12)

$$\begin{pmatrix} k & k' \\ \ell & \ell' \end{pmatrix} = \iint \psi_k^{*(1)} \psi_{k'}^{*(2)} \left(\frac{1 - P_{12}}{r_{12}} \right) \psi_\ell^{(1)} \psi_{\ell'}^{(2)} dv_1 dv_2 ,$$

where $\int dv_i$ denotes integration over both space and spin coordinates of electron i . Letting $K = (k_1, k_2, \dots, k_N)$, the diagonal elements of $\underline{\underline{H}}_{\underline{\underline{\Psi}}}$ may be expressed

$$(5.13) \quad H_{KK} = \sum_{i=1}^N \left\{ \begin{pmatrix} k_i \\ k_i \end{pmatrix} + \sum_{j=i+1}^N \begin{pmatrix} k_i & k_j \\ k_i & k_j \end{pmatrix} \right\} \quad .$$

If the sets K and L differ by just one orbital, k in K and ℓ in L ,

$$(5.14) \quad H_{KL} = (-1)^{s_{k\ell}^{KL}} \left\{ \begin{pmatrix} k \\ \ell \end{pmatrix} + \sum_{\substack{i=1 \\ k_i \neq k}}^N \begin{pmatrix} k & k_i \\ \ell & k_i \end{pmatrix} \right\}$$

where $s_{k\ell}^{KL}$ is the number of interchanges required in the set L to bring ℓ to the position of k in the set K . If K and L differ in two orbitals k, k' in K and ℓ, ℓ' in L ,

$$(5.15) \quad H_{KL} = (-1)^{s_{kk'\ell\ell'}^{KL}} \begin{pmatrix} k & k' \\ \ell & \ell' \end{pmatrix}$$

where $s_{kk'\ell\ell'}^{KL}$ is the number of interchanges in L necessary to bring ℓ and ℓ' to the positions of k and k' , respectively, in K . If K and L differ in more than two orbitals, then

$$(5.16) \quad H_{KL} = 0.$$

6. Spin and σ_v Projection Operators

Now it remains to apply the projection operators for the spin and (if $L_z = 0$) σ_v operators to determine the matrices A and P in (5.11). Of the various methods for forming pure spin functions, the one which seems most suitable for automatic machine computation is that given by Löwdin* and used here.

Let the occupation numbers,

$$n_1, n_2, \dots; \quad n_i = 0, 1, \text{ or } 2; \quad \sum_i n_i = N,$$

* See Page 21, Ref. [21].

of a Slater determinant (SD) give the number of times the respective MO's ϕ_1, ϕ_2, \dots appear in it and let $\{\underline{\Psi}_K\}$ denote the list of all SD's having a given set of occupation numbers and a given eigenvalue s_z of \mathcal{S}_z . The notation $\{K\}$ will denote the list of ordered sets K corresponding to the SD's $\{\underline{\Psi}_K\}$. The number of α electrons, μ , and the number of β electrons, ν , in the singly occupied MO's of the SD's in $\{\underline{\Psi}_K\}$ satisfy

$$(6.1) \quad 2s_z = \mu - \nu$$

$$(6.2) \quad N_s = \mu + \nu$$

where N_s is the number of singly-occupied MO's. The procedure given here will project, from $\{\underline{\Psi}_K\}$, all the eigenfunctions of \mathcal{S}^2 having $s = s_z$. The multiplicity of the corresponding eigenvalue $s(s+1)$ is

$$(6.3) \quad M = 2s + 1 .$$

The list of SD's $\{\underline{\Psi}_K\}$, which can be described by listing all ways of distributing μ α -spins and ν β -spins over the N_s singly occupied MO's, will be assumed to be in alphabetical order, i.e., the order in which the list $\{\underline{\Psi}_K\}$ would appear in a Greek dictionary if just the α 's and β 's for each SD were written. For example, if

$N_s = 5$ and a doublet state, i.e., $M = 2$, is desired, then $s = \frac{1}{2}$, $\mu = 3$, and $v = 2$. The SD's $\{\Psi_K\}$ for this case are listed in the first column of Table 1. It is already known that with this ordering, the spin projections of the first

$$(6.4) \quad \frac{M}{\mu+1} \binom{N_s}{\mu}$$

SD's in $\{\Psi_K\}$ give the maximum number of linearly independent projections of the whole set. There are, therefore, five independent doublet states in the present example. The projection operator which projects the s-state component out of a determinantal wave function having $s_z = s$ can be written*

$$(6.5) \quad \mathcal{O}_s[\alpha^\mu | \beta^v] = \frac{M}{\mu+1} \sum_{p=0}^v (-1)^p \binom{\mu}{p}^{-1} [\alpha^{\mu-p} \beta^p | \alpha^p \beta^{v-p}] ,$$

where the bracketed expression in the p -th term is the sum of all SD's obtained by exchanging p α -spins for β -spins in the SD

$$(6.6) \quad \overbrace{\alpha \dots \alpha}^{\mu} \overbrace{\beta \dots \beta}^v .$$

* Equation A11, of Ref. [21].

TABLE 1. INDEPENDENT SPIN PROJECTIONS FOR FIVE
UNPAIRED ELECTRONS IN A DOUBLET STATE

$\underline{\Psi}_K$	$\mathcal{O}_S \alpha\alpha\alpha\beta\beta$	$\mathcal{O}_S \alpha\alpha\beta\alpha\beta$	$\mathcal{O}_S \alpha\alpha\beta\beta\alpha$	$\mathcal{O}_S \alpha\beta\alpha\alpha\beta$	$\mathcal{O}_S \alpha\beta\alpha\beta\alpha$
$\alpha\alpha\alpha\beta\beta$	1/2	-1/6	-1/6	-1/6	-1/6
$\alpha\alpha\beta\alpha\beta$	-1/6	1/2	-1/6	-1/6	1/6
$\alpha\alpha\beta\beta\alpha$	-1/6	-1/6	1/2	1/6	-1/6
$\alpha\beta\alpha\alpha\beta$	-1/6	-1/6	1/6	1/2	-1/6
$\alpha\beta\alpha\beta\alpha$	-1/6	1/6	-1/6	-1/6	1/2
$\alpha\beta\beta\alpha\alpha$	1/6	-1/6	-1/6	-1/6	-1/6
$\beta\alpha\alpha\alpha\beta$	-1/6	-1/6	1/6	-1/6	1/6
$\beta\alpha\alpha\beta\alpha$	-1/6	1/6	-1/6	1/6	-1/6
$\beta\alpha\beta\alpha\alpha$	1/6	-1/6	-1/6	1/6	1/6
$\beta\beta\alpha\alpha\alpha$	1/6	1/6	1/6	-1/6	-1/6

The elements of the \underline{C} matrix for the spin projection operator, which appear as the coefficients in (6.5) may be expressed in the form

$$(6.7) \quad c_{KL} = \frac{M}{\mu+1} (-1)^{p_{KL}} \binom{\mu}{p_{KL}}^{-1}$$

where p_{KL} is the number of spin interchanges required to change $\underline{\Psi}_K$ into $\underline{\Psi}_L$. Application of this procedure

to the first five SD's of the list in the example gives the matrix of coefficients in Table 1. The table is arranged so that the K-th column, $K = 1, \dots, 5$, gives the spin projection of the K-th SD. If $L_z \neq 0$, \underline{C} need only be orthonormalized to give the matrices \underline{A} and \underline{P} in (5.11).

Now, suppose that a rectangular \underline{C} matrix is formed by the above procedure and that $L_z = 0$. Then, one must apply the projection operator

$$(6.8) \quad \sigma_v = \frac{1}{2}(1 \pm \sigma_v)$$

where + is used for a \sum^+ state and - is used for a \sum^- state. It is desirable to express the effect of σ_v in terms of the elements of \underline{C} , i.e., without requiring coefficients of the linearly dependent spin projections. The effect of σ_v on the SD's $\{\underline{\psi}_K\}$ is to replace the occupied MO's by their complex conjugates. Due to the convention, adopted here, of keeping the indices of both the MO's and the MSO's in numerical order (2.7), the sign change, which may result from putting the conjugates of the MSO's in this order after operating with σ_v , is the same for the whole set $\{\underline{\psi}_K\}$. The effect of σ_v can be expressed

$$(6.9) \quad \sigma_v \{ \underline{\psi}_K \} = \{ \underline{\psi}_K^* \} = \pm \{ \underline{\psi}_{K'} \} .$$

This relation defines a one-one correspondence between the list of ordered sets $\{ K \}$ and the list of ordered sets $\{ K' \}$. Let $|\sigma_v|$ be defined by

$$(6.10) \quad |\sigma_v| \{ \underline{\psi}_K \} = \{ \underline{\psi}_{K'} \} .$$

Since $\sigma_v^2 = 1$,

$$(6.11) \quad |\sigma_v| \{ \underline{\psi}_{K'} \} = \{ \underline{\psi}_K \} .$$

Therefore, when σ_v operates on the SD's in $\{ \underline{\psi}_K \}$, it can be expressed

$$(6.12) \quad \sigma_v = \frac{1}{2}(1 + \text{sgn } |\sigma_v|)$$

where $\text{sgn} = \pm 1$ is the product of the alternative signs in (6.8) and (6.9). Now let

$$(6.13) \quad \sigma = \sigma_s \sigma_v = \sigma_v \sigma_s .$$

The second equality holds because \mathcal{S}^2 and σ_v commute.

If the operation σ_v changes the occupation numbers of $\{ \underline{\psi}_K \}$, then the lists $\{ \underline{\psi}_K \}$ and $\{ \underline{\psi}_{K'} \}$ have no SD's in common. The result of applying σ_v to the spin function

$$(6.14) \quad \mathcal{O}_S \underline{\Psi}_K = \sum_{L \in \{K\}} \underline{\Psi}_L C_{LK}$$

is

$$(6.15) \quad \mathcal{O} \underline{\Psi}_K = \sum_{L \in \{K\}} \left(\underline{\Psi}_L \frac{1}{2} C_{LK} + \underline{\Psi}_L, \operatorname{sgn} \frac{1}{2} C_{LK} \right) .$$

On the other hand, if σ_v does not change the occupation numbers, the lists $\{\underline{\Psi}_K\}$ and $\{\underline{\Psi}_{K'}\}$ have the same SD's in, perhaps, a different order. In this case, (6.14) can also be written,

$$(6.16) \quad \mathcal{O}_S \underline{\Psi}_K = \sum_{L' \in \{K'\}} \underline{\Psi}_{L'} C_{L'K} .$$

Using both (6.14) and (6.16), and the relation (6.11), one gets

$$\begin{aligned} \mathcal{O} \underline{\Psi}_K &= \frac{1}{2} \left\{ \sum_{L \in \{K\}} \underline{\Psi}_L C_{LK} + \operatorname{sgn} |\sigma_v| \sum_{L' \in \{K'\}} \underline{\Psi}_{L'} C_{L'K} \right\} \\ &= \frac{1}{2} \left\{ \sum_{L \in \{K\}} \underline{\Psi}_L C_{LK} + \operatorname{sgn} \sum_{L' \in \{K'\}} \underline{\Psi}_{L'} C_{L'K} \right\} . \end{aligned}$$

Therefore,

$$(6.17) \quad \mathcal{O} \underline{\Psi}_K = \sum_{L \in \{L\}} \underline{\Psi}_L \frac{1}{2} (C_{LK} + \operatorname{sgn} C_{L'K}) .$$

The coefficients of the SD's in (6.15) or (6.17), as the case may be, give the \underline{C} matrix of (5.9) for the operator \mathcal{O} . When calculating the matrices \underline{A} and \underline{P}

of (5.11) by the orthogonalization procedure, the dependent projections resulting from the application of \mathcal{O}_v are found and discarded.

7. The Machine Program For Constructing Pure State Wave Functions

The I.B.M. 704, for which these calculations have been programmed, has certain Boolean operations which treat the 36-bit binary words as sets. That is, a 1 or 0 in bit position n can mean that object number n is or is not in the set. Letting A and B be two sets represented in this fashion, a single machine operation can compute their intersection,

$$C = A * B ,$$

which is a word having 1's where both A and B have 1's and 0's elsewhere. Another operation gives the union of A and B ,

$$C = A + B ,$$

which is a word having 1's where either A or B have 1's and 0's elsewhere. The complement of A ,

$$C = (-A) ,$$

is formed by changing 0's to 1's, and vice-versa, in A. The notation used here for the Boolean operations is that used in programming them in the latest FORTRAN coding system.

Since the Slater determinants described above are ordered sets of objects, no one of which can appear more than once, it is convenient to represent them by binary words with 0 or 1 representing the absence or presence of a function in the determinant. The Boolean operations then enable one to perform tests and operations on these sets. Specifically, an SD is represented in the first twenty bits of a word with bit positions corresponding to the twenty one-electron functions,

$$\begin{aligned}
 &1\sigma_g\alpha, 1\sigma_g\beta, 1\sigma_u\alpha, 1\sigma_u\beta, 2\sigma_g\alpha, 2\sigma_g\beta, 2\sigma_u\alpha, \\
 (7.1) \quad &2\sigma_u\beta, 3\sigma_g\alpha, 3\sigma_g\beta, 3\sigma_u\alpha, 3\sigma_u\beta, \pi_g^-\alpha, \pi_g^-\beta, \\
 &\pi_u^-\alpha, \pi_u^-\beta, \pi_g^+\alpha, \pi_g^+\beta, \pi_u^+\alpha, \pi_u^+\beta,
 \end{aligned}$$

in that order. For example, the bit pattern

$$A = 1011010 \dots 0$$

represents the determinant

$$A = (4!)^{-\frac{1}{2}} \det \{1\sigma_g\alpha, 1\sigma_u\alpha, 1\sigma_u\beta, 2\sigma_g\beta\}.$$

To illustrate how tests and operations are performed, consider the formation of $|\sigma_v|A$, the complex conjugate, without sign, of a determinant A . The operation $|\sigma_v|$ simply replaces each π^\pm by π^\mp and can be performed by shifting the contents of the four π^+ bit positions to the four π^- positions, and vice-versa. To observe the specific steps involved, let TS , TM , and TP be words having 1's in the σ , π^- , and π^+ positions, respectively, and 0's elsewhere. Then, using Boolean operations, the machine forms

$$\begin{aligned}
 AS &= A * TS \\
 (7.2) \quad AM &= A * TP \text{ shifted left } 4 \\
 AP &= A * TM \text{ shifted right } 4 .
 \end{aligned}$$

Then $|\sigma_v|A$ is

$$(7.3) \quad AS + AM + AP .$$

The sign in equation (6.9) is just

$$(7.4) \quad (-1)^{(\mathcal{N}(AM)\mathcal{N}(AP))}$$

where \mathcal{N} is a function which computes the number of 1's in a word. In the same notation, the calculation of the eigenvalue of \mathcal{L}_z can be described by the formula

$$(7.5) \quad L_z = \mathcal{N}(\text{AP}) - \mathcal{N}(\text{AM}) .$$

The program for computing the pure state wave functions accepts as input, N , the number of electrons, M , the multiplicity, and the eigenvalues of the three operators \mathcal{L}_z , \mathcal{L} , and \mathcal{S}_v . The multiplicity determines the eigenvalues of \mathcal{L}^2 and \mathcal{L}_z . The number of occupied orbitals, N_o , can assume all integral values such that

$$(7.6) \quad I \leq N_o \leq \text{Min} (10, N)$$

where I is the integral part of $\frac{1}{2}(N+1)$. For each N_o , which can be considered fixed for the rest of the present discussion, the program calculates the number of doubly and singly occupied orbitals,

$$N_d = N - N_o$$

and

$$N_s = N_o - N_d ,$$

respectively. The numbers of α and β electrons in the singly occupied MO's are

$$\mu = \frac{1}{2}(N_s + M - 1)$$

and

$$\nu = N_s - \mu ,$$

respectively. To form the bit patterns for the SD's, a subroutine was written which accepts a given M_1 and M_2 and generates a list of $\binom{M_2}{M_1}$ binary words; one word for each way of distributing M_1 1's among the first M_2 bit positions. The list would be in alphabetical order if 1 and 0 were α and β , respectively. This subroutine is used to generate three lists, D, S, and A with elements

$$\begin{aligned}
 & D_i, \quad i = 1, 2, \dots, \binom{10}{N_d} \\
 (7.7) \quad & S_j, \quad j = 1, 2, \dots, \binom{10-N_d}{N_s} \\
 & A_k, \quad k = 1, 2, \dots, \binom{N_s}{\mu}.
 \end{aligned}$$

The list D gives all ways of selecting N_d doubly occupied MO's from the ten available ones, S gives all ways of selecting N_s singly occupied MO's from among the $10-N_d$ remaining MO's, and A gives all ways of distributing μ α -spins over the N_s singly occupied MO's. The triplets D_i, S_j, A_k , with i, j, k , going over the ranges in (7.7) describe all SD's having N_o occupied MO's.

The \underline{C} matrix for the spin projection operator, which will be denoted by \underline{C}_S , depends only on A ; not on D and S . The elements of \underline{C}_S are calculated by using (6.7) where p_{KL} is simply the number of 1's in the result of the Boolean operation

$$A_k * (-A_\ell)$$

on the spin patterns A_k and A_ℓ of K and L . This is simply a way of counting the number of positions where A_k has α and A_ℓ has β . If $L_Z \neq 0$, then \underline{C}_S is orthonormalized, yielding the matrices \underline{A} and \underline{P} of (5.11) for an, as yet, unspecified set of MO's. Otherwise, \underline{C}_S is saved.

Then, for each i, j in the ranges defined by (7.7), D_i and S_j are examined to see if they give SD's having the required eigenvalues of \mathcal{L}_Z and i . If not, the program goes on to the next i, j . Otherwise, a subroutine combines D_i, S_j with A_k for $k = 1, 2, \dots, \binom{N_S}{\mu}$, to form a list $\{\underline{\Psi}_K\}$ in terms of bit patterns according to the scheme in (7.1). If $L_Z \neq 0$, the \underline{A} and \underline{P} matrices, which were calculated for the \underline{C}_S matrix and saved, give the result in the form required by (5.11). Otherwise, the \mathcal{O}_v operator is applied by the use of equations (6.15) or (6.17). This involves simple row

operations on \underline{C}_s and the formation of the complex conjugates $\{\underline{\Psi}_K\}$ by the operations described in (7.2) and (7.3). The \underline{C} matrix resulting from these operations on \underline{C}_s is then orthonormalized, dependent columns are discarded, and the \underline{A} and \underline{P} matrices required by (5.11) are calculated.

The list $\{\underline{\Psi}_K\}$, together with the list $\{\underline{\Psi}_K\}$ if $L_Z = 0$, will be called a "configuration". From the above, it is seen that the result of operating on any SD of a configuration with \mathcal{O} is a linear combination of SD's in that configuration only. Therefore, the \underline{A} and \underline{P} matrices of (5.11) can be partitioned by the configurations so that they appear as block diagonal matrices. Treatment of them as such produces a great saving in storage and calculation.

The elements of $\underline{H}\underline{\Psi}$ in (5.11) are calculated by subroutines which use the Boolean operations to examine the bit patterns for the $\underline{\Psi}_K$'s in the book-keeping process which selects the one- and two-electron integrals needed in equations (5.13), (5.14), and (5.15).

In order to perform the elimination of dependent projections, it is necessary to detect the presence of identically-zero matrix elements during the calculation. This means that an exact representation of all numbers

must be carried throughout the calculation. To do this, the matrix elements, which are rational numbers a/b are represented in the machine as pairs of integers (a,b) and the calculations are performed in integer arithmetic by FORTRAN subroutines written for the purpose.

8. Averaging Over Electronic Coordinates

Nearly all important properties and perturbation theory estimates of weak interactions are given at each fixed R in terms of integrals of the form

$$(8.1) \quad P(R) = \int \underline{\Psi}^* \mathcal{P} \underline{\Psi}' dV$$

where \mathcal{P} is a sum of mono-electronic operators

$$(8.2) \quad \mathcal{P} = \sum_{i=1}^N \mathcal{P}(i)$$

and $\underline{\Psi}$ and $\underline{\Psi}'$ are two wave functions for the system.

If $\underline{\Psi} = \underline{\Psi}'$, then (8.1) gives the average value of \mathcal{P} when the system is in a situation characterized by the normalized wave function $\underline{\Psi}$. If $\underline{\Psi} \neq \underline{\Psi}'$, (8.1) gives information about the system in a transition from the state $\underline{\Psi}$ to the state $\underline{\Psi}'$. The integral (8.1) for any operator of the form (8.2) can be obtained in terms of the function

$$(8.3) \quad \rho(1',1) = N \int \underline{\Psi}^*(1',2,\dots,N) \underline{\Psi}'(1,2,\dots,N) dV^{(1)} ,$$

where $\int dV^{(1)}$ denotes integration over all electronic coordinates except those of electron 1. If $\underline{\Psi} = \underline{\Psi}'$, (8.3) is called the "density matrix" and if $\underline{\Psi} \neq \underline{\Psi}'$, it is called the "transition matrix". In this section, we need not distinguish between the two. If $1' = 1$, and $\underline{\Psi} = \underline{\Psi}'$, (8.3) gives the density of electronic charge at the point corresponding to the space-spin coordinates 1. The primed one-electron coordinates are used to allow for operators on the phase space of the system.

The integral (8.1) can then be given in terms of $\rho(1',1)$ by

$$(8.4) \quad \int \mathcal{P}(1) \rho(1',1) dv_1 ,$$

where the notation implies that $\mathcal{P}(1)$ is to operate on only the unprimed coordinates of $\rho(1',1)$ after which the primes are removed and the integration is performed.

To get $\rho(1',1)$ in terms of the MSO's ψ_1, ψ_2, \dots , consider the form of the wave function involved,

$$(8.5) \quad \underline{\Psi} = \sum_K c_K \underline{\Phi}_K .$$

The $\underline{\Phi}_K$'s are the pure state functions in (5.10),

$$(8.6) \quad \underline{\Phi}_K = \sum_L \underline{\Psi}_L A_{LK} ,$$

so that (8.5) can be written

$$(8.7) \quad \underline{\Psi} = \sum_L B_L \underline{\Psi}_L$$

where

$$(8.8) \quad B_L = \sum_K A_{LK} C_K .$$

Hence, (8.3) can be written

$$(8.9) \quad \rho(1', 1) = N \sum_{K, L} B_K B'_L \int \underline{\Psi}_K^* \underline{\Psi}'_L dV^{(1)} .$$

In order to evaluate (8.9), one needs the following relation:

$$\begin{aligned} & \int \det \{ \psi_1^*(1), \dots, \psi_M^*(M) \} \det \{ \psi_1'(1), \dots, \psi_M'(M) \} dv_1 \dots dv_M \\ &= M! \int \psi_1^*(1), \dots, \psi_M^*(M) \det \{ \psi_1'(1), \dots, \psi_M'(M) \} dv_1 \dots dv_M \\ &= M! \int \det \{ \psi_1^*(1) \psi_1'(1), \dots, \psi_M^*(M) \psi_M'(M) \} dv_1 \dots dv_M \\ (8.10) \quad &= M! \begin{vmatrix} S_{11} & \dots & S_{1M} \\ \vdots & & \vdots \\ S_{M1} & \dots & S_{MM} \end{vmatrix} , \end{aligned}$$

where

$$(8.11) \quad S_{k\ell} = \int \psi_k^*(1) \psi_\ell'(1) dv_1 .$$

Expanding the determinants in (8.9) in terms of their first rows, one obtains,

$$(8.12) \quad \rho(1',1) = [(N-1)!]^{-1} \sum_{K,L} B_K B_L' \sum_{i,j=1} \psi_{k_i}^*(1') \psi_{\ell_j}'(1) \\ \times \int d_K(k_i) d_L'(\ell_j) dV^{(1)} ,$$

where $K = (k_1, \dots, k_N)$ and $L = (\ell_1, \dots, \ell_N)$ and where $d_K(k_i)$ is $(-1)^{i+1}$ times the first minor of the element $\psi_{k_i}(1)$ in the SD $\underline{\psi}_K$. By the relation (8.10), it is seen that

$$(8.13) \quad \int d_K(k_i) d_L'(\ell_j) dv_2 \dots dv_N = (N-1)! D_{k_i \ell_j}^{KL} ,$$

where $D_{k_i \ell_j}^{KL}$ is $(-1)^{i+j}$ times the first minor of the k_i, ℓ_j element of the determinant of the "overlap" matrix

$$(8.14) \quad \underline{S} = \begin{pmatrix} S_{k_1 \ell_1} & \dots & S_{k_1 \ell_N} \\ \vdots & & \\ S_{k_N \ell_1} & \dots & S_{k_N \ell_N} \end{pmatrix}$$

whose elements are defined by (8.11). Hence,

$$(8.15) \quad \rho(1',1) = \sum_{K,L} B_K B_L' \sum_{i,j=1}^N D_{k_i \ell_j}^{KL} \psi_{k_i}^*(1') \psi_{\ell_j}'(1) .$$

Changing the order of summation in (8.15) gives

$$(8.16) \quad \rho(1',1) = \sum_{k,\ell} \Gamma_{k\ell} \psi_k^*(1') \psi_\ell'(1)$$

where

$$(8.17) \quad \Gamma_{k\ell} = \sum_{K \in (k)} \sum_{L \in (\ell)} B_K B_L' D_{k\ell}^{KL}.$$

The summation is over all K containing k and all L containing ℓ .

The integral (8.1) can then be expressed in the form

$$(8.18) \quad P(R) = \sum_{k,\ell} \Gamma_{k\ell} \int \psi_k^*(1') \rho(1) \psi_\ell'(1) dv_1$$

in terms of one-electron integrals. The sum in (8.17) can be formed by going over all pairs of determinants $\underline{\Psi}_K$, $\underline{\Psi}_L'$ and including the K,L term of (8.17) in the sum for each $\Gamma_{k\ell}$ for which $k \in K$ and $\ell \in L$. In the scheme for representing SD's as bit patterns, as described in Section 7, a simple Boolean " $*$ " operation is used to test for the presence of an MO ψ_k in a determinant $\underline{\Psi}_K$.

If the one-electron MO's used in constructing $\underline{\Psi}$ belong to the same orthonormal set as those used in constructing $\underline{\Psi}'$, then

$$(8.19) \quad S_{k\ell} = \delta_{k\ell}$$

and, therefore,

$$(8.20) \quad D_{k\ell}^{KL} = \delta_{K-k, L-\ell} (-1)^{s_{k\ell}^{KL}}$$

where $K-k$ and $L-\ell$ denote the sets K with k omitted and L with ℓ omitted and $s_{k\ell}^{KL}$ is defined in (5.14).

In the special case of properties for which \mathcal{P} commutes with the operators whose projection operators were used in obtaining the Φ_K 's, a simplification is available which amounts to allowing one to use C_K instead of B_K in (8.17) to calculate a set of $\Gamma_{k\ell}$'s which can be used in (8.18) to calculate the average value of \mathcal{P} .

9. Optimization of Non-Linear Parameters

The calculation of optimal linear parameters of a trial wave function for a given pure state consists in solving the matrix eigenvalue equation

$$(9.1) \quad \sum_L (H_{KL} - \delta_{KL} E) C_L = 0$$

where H_{KL} is the matrix of the Hamiltonian of the system with respect to a set of orthonormal pure state functions Φ_K , $K = 1, 2, \dots$. The eigenvalues, $E_0 \leq E_1 \leq E_2 \leq \dots$, and their corresponding eigenfunctions,

$$(9.2) \quad \underline{\Psi}_v = \sum_L c_L^{(v)} \underline{\Phi}_L, \quad v = 1, 2, \dots,$$

are approximations to the eigenvalues and eigenfunctions of the wave equation (1.1) for the pure state under consideration. Furthermore, according to the general separation theorem* [23], E_v is an upper bound of the eigenvalue it approximates. This procedure optimizes the linear parameters c_L of the wave function, but one must also consider non-linear parameters such as the orbital exponents of the AO's.

Letting μ represent any set of non-linear parameters in the wave function, the eigenvalues of (9.1) may be regarded as functions $E_v(\mu)$ of μ . Then, since $E_v(\mu)$ is an upper bound to the v -th exact eigenvalue, one can improve $E_v(\mu)$, for some particular value of v , by finding the point $\mu = \mu_v$ where $E_v(\mu)$ attains a minimum. The corresponding wave functions, $\underline{\Psi}_v(\mu)$, $v = 1, 2, \dots$,

* A rough outline of a proof of the separation theorem can be formulated by regarding Equation (4.1) of Chapter IV, below, as the matrix formulation of (9.1). The results in Chapter IV show that if the basis functions for (9.1) are taken from a complete set of functions, the addition of one more function gives a new set of eigenvalues such that, except for the maximum one, each is lower than or equal to an eigenvalue of the previous set. Therefore, the addition of functions of the complete set, one by one, yields a non-increasing sequence of approximations to each exact eigenvalue.

are orthogonal to each other if all have the same μ , but the optimized wave functions $\underline{\Psi}_v(\mu_v)$ will, in general, not have this property. This means that in the calculation of transition matrix elements and perturbations one will, at least in effect, use wave functions which are orthogonal, but less accurate than the $\underline{\Psi}_v(\mu_v)$'s. In the case of perturbation calculations, the favorable aspect of such a procedure is that one can select and optimize a particular eigenstate for the unperturbed system and, if the perturbation is small, the effect of the non-orthogonality will also be small. However, the projection operators do not depend upon μ , so the wave functions $\underline{\Psi}_v(\mu_v)$ will be orthogonal to the eigenfunctions for other pure states.

The calculation of electronic wave functions for even a single set of non-linear parameters requires a considerable amount of calculation and one will, in practical applications, be quite limited in the number of such parameters one can vary and in the number of eigenvalues one can optimize. Thus, the convenience of using the small number of basis functions in the calculations described here is somewhat lessened by the fact that the orbital exponents are quite critical in the determination of energies and other molecular properties. This

necessitated putting a somewhat large amount of computational effort into the procedure, described in the next section, for minimizing a function of several variables.

10. Numerical Method for Minimizing a Function of n Variables

In numerical work, one frequently encounters the problem of having to determine a point where a given function $F(\underline{v})$, $\underline{v} = (v_1, v_2, \dots, v_n)$, whose values can be calculated, attains a minimum. The amount of computing effort involved in obtaining a detailed knowledge of the behavior of a function of several variables from its numerical values can be formidable if one does not employ an effective means of utilizing the information obtained in successive evaluations of the function. The computing machine subroutine described in this section uses a process of fairly general applicability for finding a relative minimum point of a given function. The procedure is best described by first giving a brief outline of its essential features. On each iteration, a quadratic function^{*}, $G(\underline{v})$, coincident with $F(\underline{v})$ at the best

^{*} Some basic ideas for fitting and using quadratic surfaces for minimizing a function of several variables are discussed in Ref. [24].

$$(10.1) \quad m = \frac{1}{2}(n+1)(n+2)$$

calculated values of $F(\underline{v})$, is obtained by determining the m coefficients of

$$(10.2) \quad G(\underline{v}) = a + \underline{b}^{\dagger} \underline{v} + \frac{1}{2} \underline{v}^{\dagger} \underline{C} \underline{v},$$

where \underline{b} and \underline{v} are column vectors, \underline{C} is a symmetric matrix, and " \dagger " denotes the transpose. The symmetric matrix \underline{C} is diagonalized, giving the eigenvalues C_i' , $i = 1, 2, \dots, n$ of \underline{C} . If the points used to determine (10.2) are in a sufficiently small neighborhood of a minimum point of $F(\underline{v})$, then $C_i' > 0$ for $i = 1, 2, \dots, n$ and the minimum point of (10.2) gives a good approximation to the minimum point of $F(\underline{v})$. If the condition $C_i' > 0$, $i = 1, 2, \dots, n$ does not hold, a new point is found by going from the best calculated point in the direction of the negative gradient of $G(\underline{v})$ at that point.

To start the iterative procedure, the program is given an initial point \underline{v}_0 and positive step-sizes, d_1, \dots, d_n , for all variables. Then $F(\underline{v})$ is calculated at $\underline{v}_0 = (v_{10}, \dots, v_{n0})$ and at the $2n$ points $(v_{10}, \dots, v_{i0} \pm d_i, \dots, v_{n0})$, $i = 1, 2, \dots, n$. From these computed values,

$$S_i = - \operatorname{sign} [F(v_{10}, \dots, v_{i0} + d_i, \dots, v_{n0}) \\ - F(v_{10}, \dots, v_{i0} - d_i, \dots, v_{n0})]$$

is determined and $F(\underline{v})$ is calculated at the $\frac{1}{2}n(n-1)$ points $(v_{10}, \dots, v_{i0} + S_i d_i, \dots, v_{j0} + S_j d_j, \dots, v_{n0})$. This provides the m points needed to fit the first quadratic surface.

On each iteration, the program has an ordered list of points \underline{v}_j and calculated values $G_j = F(\underline{v}_j)$, $j = 1, 2, \dots, m'$, where $m' = m$ or $m+1$, such that $G_1 \leq G_2 \leq \dots \leq G_{m'}$. The m independent coefficients of (10.2) are determined by the m' equations

$$(10.3) \quad G_j = G(\underline{v}_j), \quad j = 1, 2, \dots, m'.$$

As it will be shown, the rank of the system of equations (10.3) is at least m at the start of each iteration.

Equations (10.3) are solved by the Gauss elimination method, taking them in the order $j = 1, 2, \dots$. By this method, the vanishing of the coefficients of the ℓ -th equation during the elimination process implies that the ℓ -th equation is redundant or inconsistent. In this case, the ℓ -th point is discarded from the list and the $\ell+1, \ell+2, \dots, m'$ points in the list and the corresponding equations in (10.3) are re-numbered $\ell, \ell+1, \dots, m'-1$. If

$m' = m+1$ and the first m equations of (10.3) are of rank m , then the $(m+1)$ -st equation is simply not used. A necessary and sufficient condition that $G(\underline{v})$ have a minimum at a point is that the gradient

$$(10.4) \quad \nabla G(\underline{v}) = \underline{b} + \underline{C} \underline{v}$$

be zero and that the eigenvalues of \underline{C} satisfy

$$(10.5) \quad C_i' > 0, \quad i = 1, 2, \dots, n,$$

at the point. Therefore, the matrix \underline{C} is diagonalized, yielding an orthonormal matrix \underline{R} , whose columns are the eigenvectors of \underline{C} , and a diagonal matrix \underline{C}' whose i -th diagonal element is the eigenvalue of \underline{C} corresponding to the i -th column of \underline{R} . Hence

$$(10.6) \quad \underline{C} = \underline{R} \underline{C}' \underline{R}^{\dagger}.$$

If all of the eigenvalues of \underline{C} are positive, then the minimum point,

$$(10.7) \quad \underline{\bar{v}} = -\underline{C}^{-1} \underline{b} = -\underline{R} \underline{C}'^{-1} \underline{R}^{\dagger} \underline{b},$$

of $G(\underline{v})$ is calculated. If $\underline{\bar{v}}$ is within a distance d , to be defined later, of the best calculated point, \underline{v}_1 , then \underline{v}' , the next point at which to calculate $F(\underline{v})$, is

set equal to \bar{v} . Otherwise, the gradient (10.4) is evaluated at \underline{v}_1 and \underline{v}' is taken as the point at a distance d from \underline{v}_1 down the gradient $\nabla G(\underline{v}_1)$. Thus,

$$(10.8) \quad \underline{v}' = \underline{v}_1 - d \nabla G(\underline{v}_1) / |\nabla G(\underline{v}_1)| , \quad .$$

where $|\nabla G(\underline{v}_1)|$ denotes the length of the gradient.

On the first iteration, and on each iteration for which the previous one gave an improvement, the parameter d is the distance between the two best calculated points. If the previous iteration did not yield an improvement and if \underline{v}' of the previous iteration was obtained by going down a gradient, it is evident that d was too large and the new d is taken as half the d of the previous iteration. In the only remaining situation, where \underline{v}' of the previous iteration was obtained as the minimum point of a quadratic surface and did not yield an improvement, the old d is used.

Then, $F(\underline{v}')$ is calculated and the test for convergence, as described below, is applied. If the convergence criteria are not satisfied and if $F(\underline{v}') \leq G_m$, the new point \underline{v}' and value $F(\underline{v}')$ are placed in the appropriate place in the list of calculated values. All values G_j in the list for which $F(\underline{v}') < G_j$ are moved upward one position and renumbered. As a result of the

method of solving (10.3), the m equations (10.3), before the insertion, are of rank m . Therefore, the rank after insertion is at least m . On the other hand, if $F(\underline{v}') > G_m$, the new value is not put in the list. Instead, the calculation of a new quadratic surface is by-passed, d is replaced by $\frac{1}{2}d$, and the program goes back to the point where it uses the gradient to find a new point. In other words, it goes down the same gradient as on the previous step, but only half as far.

The usual experience is that one starts with points far apart to get the maximum searching effect of the program. Therefore, quadratic surfaces fitted in the first iterations give a poor description of the behavior of $F(\underline{v})$. Then, as the computed points begin to cluster about the region of a minimum, a fairly good description of $F(\underline{v})$ about the minimum is given by the quadratic surface, convergence becomes of second order, and the points rapidly come so close together that significance in the calculated coefficients of the quadratic surface is lost. Hence, the quadratic surface itself is not very useful in forming convergence criteria.

Among the arguments of the computer subroutine, are two parameters, NP and ϵ . If $NP > 0$, the subroutine will exit when the best NP calculated values of $F(\underline{v})$

lie within ϵ of each other. If $NP = 0$, the subroutine consults a sense switch to see if it should exit. This allows the user to use his own judgement, during a calculation, to decide when the procedure has converged. Then, if further calculations are performed with similar functions, the experience obtained should enable one to select an NP and an ϵ .

III THE CALCULATION OF MOLECULAR INTEGRALS

1. Integrals of the STO's

By performing the trivial integration over spin coordinates, one can obtain all of the integrals involved in the calculation of electronic wave functions, molecular properties, and perturbations in terms of integrals of the MO's

$$(1.1) \quad \phi_i = \sum_k \chi_k c_{ki}$$

which can, in turn, be expressed in terms of integrals of the basic set of STO's (II 4.1) on the two centers. For a one-electron operator $\mathcal{P}(1)$,

$$(1.2) \quad \int \phi_i^*(1) \mathcal{P}(1) \phi_j(1) d\tau_1 = \sum_{p,q} c_{pi} c_{qj} P_{pq}$$

where

$$(1.3) \quad P_{pq} = \int \chi_p^*(1) \mathcal{P}(1) \chi_q(1) d\tau_1 .$$

Here, $d\tau_1$ denotes integration over the space coordinates of electron 1. In particular, the one-electron integrals programmed and calculated in the course of the present work are the:

Overlap

$$(1.4) \quad \int \chi^* \chi' d\tau ,$$

kinetic energy

$$(1.5) \quad \int \chi^* \left(-\frac{1}{2} \Delta\right) \chi' d\tau ,$$

nuclear attraction

$$(1.6) \quad \int \chi^* r_a^{-1} \chi' d\tau ,$$

dipole moment

$$(1.7) \quad \int \chi^* r_a \cos \theta_a \chi' d\tau ,$$

quadrupole moment

$$(1.8) \quad \int \chi^* [r_a^2 (3 \cos^2 \theta_a - 1)/2] \chi' d\tau ,$$

electric field,

$$(1.9) \quad \int \chi^* r_a^{-2} \cos \theta_a \chi' d\tau ,$$

and electric field gradient

$$(1.10) \quad \int \chi^* r_a^{-3} (3 \cos^2 \theta_a - 1) \chi' d\tau$$

integrals, where χ and χ' are the STO's (II 4.2).

The only two-electron property considered here is the inter-electronic potential r_{12}^{-1} in the electronic energy equation. For this, one needs the integrals

$$\begin{aligned}
 & \iint \phi_i^*(1) \phi_j^*(2) r_{12}^{-1} \phi_k(1) \phi_\ell(2) d\tau_1 d\tau_2 \\
 (1.11) \quad & = \sum_{pqrs} C_{pi} C_{qj} C_{rk} C_{sl} G_{pqrs}
 \end{aligned}$$

where

$$(1.12) \quad G_{pqrs} = \iint \chi_p^*(1) \chi_q^*(2) r_{12}^{-1} \chi_r(1) \chi_s(2) d\tau_1 d\tau_2 .$$

The integrals (1.12) are usually divided into three types according to the centers of the STO's involved. This division is relevant only when considering the means of calculating or tabulating them. The three types are the:

Coulomb

$$(1.13) \quad \iint \chi_a^*(1) \chi_b'^*(2) r_{12}^{-1} \chi_a''(1) \chi_b'''(2) d\tau_1 d\tau_2 ,$$

Hybrid

$$(1.14) \quad \iint \chi_a^*(1) \chi_b'^*(2) r_{12}^{-1} \chi_a''(1) \chi_a'''(2) d\tau_1 d\tau_2 ,$$

and Exchange

$$(1.15) \quad \iint \chi_a^*(1) \chi_a'^*(2) r_{12}^{-1} \chi_b''(1) \chi_b'''(2) d\tau_1 d\tau_2 ,$$

integrals, where the subscripts a and b denote the centers A and B of the STO's. The integrals having

all AO's on the same center can be obtained from any of the above by setting R , the internuclear distance, equal to zero.

Most of the literature on the calculation of these integrals and the earlier calculations for some closed-shell systems have treated the real STO's which are defined as the real and imaginary parts of the STO's (II 4.1). The one-electron integrals are the same, whether one's notation denotes complex or real STO's, and the two-electron integrals of complex orbitals are, in general, linear combinations of the integrals of the real STO's. Therefore, the STO's discussed in this section and in the tables referred to are the real STO's.

In the Coulomb and Hybrid integrals, the charge distribution for electron 1, $\chi_a^*(1) \chi_a''(1)$, can be expanded in a finite series of real spherical harmonics on center A. Then, one can use the expansion

$$(1.16) \quad r_{12}^{-1} = \sum_{\ell=0}^{\infty} \frac{4}{2\ell+1} \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} \sum_{m=-\ell}^{m=\ell} S_{\ell m}(\theta_{a1}, \phi_1) S_{\ell m}(\theta_{a2}, \phi_2)$$

where the $S_{\ell m}$'s are the real spherical harmonics and $r_{<}$ and $r_{>}$ are the smaller and larger, respectively, of r_{a1} and r_{a2} . The integration over the coordinates of electron 1 can be carried out, yielding a finite

expression for the potential at electron 2 due to the charge distribution of electron 1. The integration over ϕ_2 can also be performed, giving a finite series of integrals over the two remaining coordinates of electron 2. In the next two sections, two alternative means of expressing and evaluating the integrals appearing in this finite series will be given.

In the exchange integrals, each electron has a charge distribution which is a product of an AO on A and an AO on B and, in general, this gives rise to an infinite series of two-dimensional integrals. While work on the integrals reported here was in progress, other workers produced and distributed a machine program for calculating the exchange integrals [25]. Hence, plans for calculating and including them here were abandoned and, instead, programs were written for calculating some of the properties for which the integrals were not available.

Three sets of tables, hereafter referred to as T I, T II, and T III, were produced as part of the present work and published separately [26]. Detailed descriptions and instructions accompany the tables and will not be repeated here.

2. The $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -Functions

The spherical polar coordinates used for defining the AO's (II 4.1) are as described in Figure 1.

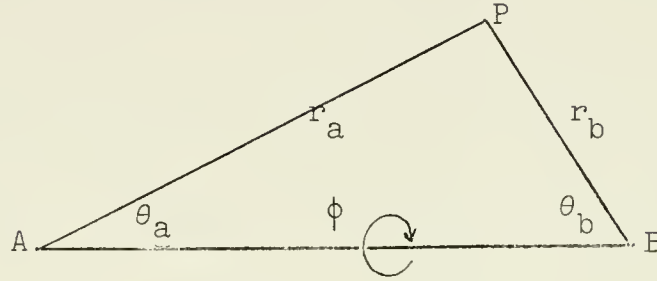


Fig. 1 -Spherical polar coordinates of electron at point P.

All of the integrals (1.4) - (1.9), (1.13), (1.14), and most of those in (1.10) can be expressed in terms of the integrals

$$C_{\alpha\beta}^{\gamma\delta\epsilon}(p,t) = \mu^K \int_0^\infty r_a^2 dr_a \int_0^\pi \sin \theta_a d\theta_a \exp(-\mu_a r_a - \mu_b r_b)$$

(2.1)

$$r_a^{\alpha+\gamma+\epsilon-1} r_b^{\beta+\delta+\epsilon-1} \cos^\gamma \theta_a \cos^\delta \theta_b \sin^\epsilon \theta_a \sin^\epsilon \theta_b$$

where

$$\begin{aligned}
 K &= \alpha + \beta + \gamma + \delta + 2\varepsilon + 1 \\
 p &= R\mu \\
 (2.2) \quad \mu &= \frac{1}{2}(\mu_a + \mu_b) \\
 t &= (\mu_a - \mu_b)/(\mu_a + \mu_b) .
 \end{aligned}$$

The integrals (2.1) exist only for $\alpha + \gamma + 2\varepsilon + 1 \geq 0$. A change to elliptic coordinates

$$\begin{aligned}
 \xi &= (r_a + r_b)/R \\
 (2.3) \quad \eta &= (r_a - r_b)/R
 \end{aligned}$$

puts the integrals (2.1) in the form

$$\begin{aligned}
 (2.4) \quad c_{\alpha\beta}^{\gamma\delta\varepsilon}(p, t) &= \left(\frac{p}{2}\right)^K \int_1^\infty d\xi \int_{-1}^1 d\eta \exp(-p\xi - pt\eta) \\
 &\quad (\xi + \eta)^\alpha (\xi - \eta)^\beta (1 + \xi\eta)^\gamma (1 - \xi\eta)^\delta (\xi^2 - 1)^\varepsilon (1 - \eta^2)^\varepsilon .
 \end{aligned}$$

These are $(1-t)^{-K}$ times the $c_{\alpha\beta}^{\gamma\delta\varepsilon}$ -functions defined by Rüdénberg , Roothaan, and Jaunzemis (hereafter referred to as RRJ) [27]. The present definition is formulated so that the relation

$$(2.5) \quad c_{\alpha\beta}^{\gamma\delta\varepsilon}(p, t) = c_{\beta\alpha}^{\delta\gamma\varepsilon}(p, -t)$$

can be used to simplify tabulation of the $c_{\alpha\beta}^{\gamma\delta\varepsilon}$ -functions.

RRJ have given recursive relations for the $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -functions which, when applied to numerical values of the functions, lose accuracy very rapidly due to "differencing effects". In a later paper, [28], Roothaan applied the recursive relations to analytic expressions, of a simple general form, for the $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -functions and gave formulas for all of the $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -functions having $\alpha \geq 0$ which are needed for the one- and two-electron integrals of the 1s, 2s, 2p σ , and 2p π AO's. A single subroutine, requiring stored arrays of polynomial coefficients for each $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -function, was written and used successfully to compute all necessary $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -functions with $\alpha \geq 0$. The procedure is extremely fast compared with others which use numerical integration and it gives high accuracy for the entire range of the parameters. By other methods, the sizes and ranges of tables T I, T II, and T III would have made the time and cost of their calculation prohibitive.

The appearance of the $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -functions with $\alpha < 0$ did present some difficulties since they are of a more complicated form, involving exponential integrals and terms having singularities. In order to avoid these complications in the calculation of the Coulomb integrals, a method was devised for expressing the linear combinations of $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -functions appearing in them with $\alpha < 0$ in terms of $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -functions with $\alpha \geq 0$.

By using $(\xi+\eta)^\alpha$ as one of the factors in two integrations by parts, with respect to ξ and η , of $C_{\alpha\beta}^{\gamma\delta 0}$, and by adding the two results, one obtains

$$(2.6) \quad (\alpha+1) C_{\alpha\beta}^{\gamma\delta 0} - \frac{\mu_a}{\mu} C_{\alpha+1,\beta}^{\gamma\delta 0} \\ = \frac{1}{p} \left\{ -\gamma C_{\alpha+2,\beta}^{\gamma-1,\delta,0} + \delta C_{\alpha+2,\beta}^{\gamma,\delta-1,0} \right\} - h_{\alpha\beta}^{\gamma+1,\delta}.$$

The functions $h_{\alpha\beta}^{\gamma\delta}$ are integrals having the property

$$(2.7) \quad h_{\alpha\beta}^{\gamma\delta} = h_{\alpha-2m,\beta-2n}^{\gamma+2m,\delta+2n}$$

for all m,n for which the corresponding integrals in (2.6) exist. Then, by doing the same thing with $(\xi-\eta)^\beta$ used as a factor in the partial integration, one obtains a formula for $h_{\alpha\beta}^{\gamma\delta}$,

$$(2.8) \quad h_{\alpha\beta}^{\gamma,\delta+1} = -(\beta+1) C_{\alpha\beta}^{\gamma\delta 0} - \frac{\mu_b}{\mu} C_{\alpha,\beta+1}^{\gamma\delta 0} \\ + \frac{1}{p} \left\{ \gamma C_{\alpha,\beta+2}^{\gamma-1,\delta,0} - \delta C_{\alpha,\beta+2}^{\gamma,\delta-1,0} \right\}.$$

Equation (2.6) gives the linear combination of $C_{\alpha\beta}^{\gamma\delta 0}$ - functions on the left side of (2.6) in terms of those with higher α . This, with formulas for raising ε , can be used to convert the linear combinations of $C_{\alpha\beta}^{\gamma\delta\varepsilon}$ -functions for

the Coulomb integrals into expressions involving $C_{\alpha\beta}^{\gamma\delta\epsilon}$'s with $\alpha \geq 0$ and $h_{\alpha\beta}^{\gamma\delta}$'s with $\alpha < 0$. Then, (2.7) can be used with convenient choices of m and n to obtain the $h_{\alpha\beta}^{\gamma\delta}$'s in terms of $h_{\alpha\beta}^{\gamma\delta}$'s with $\alpha \geq 0$. The latter are then given by (2.8) in terms of $C_{\alpha\beta}^{\gamma\delta 0}$ with $\alpha \geq 0$. Relations between the $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -functions* can then be used to simplify the final results.

The $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -functions with $\alpha < 0$ which are needed for some of the one-electron and Hybrid integrals were calculated rapidly by using explicit expressions given by Roothaan [29], but these expressions are subject to serious differencing errors in the range of parameters corresponding to small ρ (see Equations (2.2)). Therefore, for these ranges, and for some of the integrals (1.10) which cannot be expressed in terms of $C_{\alpha\beta}^{\gamma\delta\epsilon}$ -functions, the slower but more accurate methods of the next section had to be used.

3. Barnett-Coulson Zeta-functions

The basis of the Barnett-Coulson Zeta-function method [30] is the use of the expansion

$$(3.1) \quad r_b^{m-1} e^{-\beta r_b} = \beta^{-m+1} \sum_{n=0}^{\infty} (2n+1) (t\tau)^{-\frac{1}{2}}$$

$$P_n(\cos \theta_a) \zeta_{mn}(1, t; \tau)$$

* See Page 213, Ref. [27].

where

$$t = \beta r_a$$

$$\tau = \beta R$$

and where P_n is the n -th Legendre polynomial. The functions ζ_{mn} are defined by recursive relations which start with the functions

$$(3.2) \quad \zeta_{0n} = I_{n+\frac{1}{2}}(t_<) K_{n+\frac{1}{2}}(t_>)$$

where $t_>$ and $t_<$ are the larger and smaller, respectively, of t and τ and where $I_{n+\frac{1}{2}}$ and $K_{n+\frac{1}{2}}$ are the Bessel functions of purely imaginary argument. The ζ_{mn} functions with $m = 0, 1$, and 2 are denoted by γ_n , p_n , and q_n .

Using (3.1) and trigonometric identities, the coordinates of an AO on center B can be expressed in terms of spherical polar coordinates on A which may then be used as the variables of integration. This enables one to express all one-electron integrals and the two-electron Coulomb and Hybrid integrals in terms of the one-dimensional integrals defined by Barnett and Coulson,

$$(3.3) \quad Z_{m,n,\ell+\frac{1}{2}}(\kappa, \tau) = \int_0^\infty e^{-\kappa t} \zeta_{mn}(1, t; \tau) t^{\ell+\frac{1}{2}} dt,$$

where κ and τ depend upon the orbital exponents and R . The Zeta-functions (3.3) with $m = 0, 1$, and 2 are denoted by $G_{n, \ell + \frac{1}{2}}$, $P_{n, \ell + \frac{1}{2}}$, and $Q_{n, \ell + \frac{1}{2}}$ respectively.

In what follows, functions are defined and formulas are written for the express purpose of using them for calculation with an automatic computer. Their formulation is, therefore, determined so as to minimize the number of machine operations, avoid overflow, and yield maximum accuracy. Consequently, some functions and formulas do not appear in the most familiar or convenient way of expressing them in ordinary mathematical text.

The functions

$$(3.4) \quad B_n(z) = \pi^{\frac{1}{2}} (2z)^{-n - \frac{1}{2}} (2n+1)! (n!)^{-1} I_{n + \frac{1}{2}}(z) e^{-z}$$

$$(3.5) \quad C_n(z) = \pi^{-\frac{1}{2}} (2z)^{n + \frac{1}{2}} [(2n+1)!]^{-1} n! K_{n + \frac{1}{2}}(z) e^z$$

$$(3.6) \quad \bar{\zeta}_{mn}(t, \tau) = (t/\tau)^{\frac{1}{2}} \zeta_{mn}(1, t; \tau) e^{t_{>} - t_{<}}$$

will be introduced and $\bar{\gamma}_n$, \bar{p}_n , and \bar{q}_n will be used to denote $\bar{\zeta}_{mn}$ for $m = 0, 1$, and 2 , respectively. By these definitions,

$$(3.7) \quad \bar{\gamma}_n(t, \tau) = (t/\tau)^{\frac{1}{2}} (t_{<}/t_{>})^{n + \frac{1}{2}} B_n(t_{<}) C_n(t_{>})$$

and Barnett and Coulson's Zeta-functions (3.3) are just $\tau^{-1/2}$ times the functions

$$(3.8) \quad \bar{Z}_{nl}^m(\kappa, \tau) = \int_0^\infty e^{-\kappa t - (t_> - t_<)} \bar{\zeta}_{mn}(t, \tau) t^\ell dt$$

with the same values of m , n , and ℓ . The \bar{Z}_{nl}^m functions with $m = 0, 1$, and 2 will be denoted by \bar{G}_{nl} , \bar{P}_{nl} , and \bar{Q}_{nl} , respectively. The recurrence relations for the barred functions defined here are the same as those given by Barnett and Coulson for the corresponding unbarred functions. The first of the recurrence relations for raising m is

$$(3.9) \quad \bar{P}_{nl} = \tau(2n+1)^{-1} (\bar{G}_{n-1, \ell+1} - \bar{G}_{n+1, \ell+1}) .$$

For convenience in deriving and expressing integrals of the AO's the functions

$$(3.10) \quad \bar{Z}_{nl}^{mk}(\kappa, \tau) = \frac{\beta^{m+\ell+1}}{2} \int_0^\infty r_a^2 dr_a \int_0^\pi \sin \theta_a d\theta_a e^{-\alpha r_a - \beta r_b} r_a^{\ell-1} r_b^{m-1} \cos^k \theta_a P_n(\cos \theta_a) ,$$

where $\kappa = \alpha/\beta$, will be introduced here. For $k = 0$, these are equal to the functions (3.8). A familiar relation among Legendre polynomials gives the formula for raising the index k ,

$$(3.11) \quad \overline{Z}_{n\ell}^{mk} = (2n+1)^{-1} \left\{ n \overline{Z}_{n-1,\ell}^{m,k-1} + (n+1) \overline{Z}_{n+1,\ell}^{m,k-1} \right\}.$$

By using one of the recurrence relations* for the ζ_{mn} - functions, one can obtain the formula for raising m ,

$$(3.12) \quad \overline{Z}_{n\ell}^{mk} = \tau^2 \overline{Z}_{n\ell}^{m-2,k} + \overline{Z}_{n,\ell+2}^{m-2,k} - 2\tau \overline{Z}_{n,\ell+1}^{m-2,k+1}.$$

To calculate the Zeta-functions (3.8), the recurrence relations (3.9) and (3.12) in m are used, starting with an array of the $\overline{G}_{n\ell}$ functions. This produces no appreciable loss in accuracy for the integrals considered here. The computation of

$$(3.13) \quad \overline{G}_{n\ell}(\kappa, \tau) = \int_0^\infty e^{-\kappa t - (t_+ - t_-)} \overline{\gamma}_n(t, \tau) t^\ell dt$$

is performed by dividing the range of integration at $t = \tau$ and expressing the result in the form

$$(3.14) \quad \overline{G}_{n\ell}(\kappa, \tau) = C_n(\tau) \overline{G}_{n\ell}^i(\kappa, \tau) + B_n(\tau) \overline{G}_{n\ell}^s(\kappa, \tau).$$

By a change in the variable of integration, one gets

$$(3.15) \quad \overline{G}_{n\ell}^i = \tau^{\ell+1} \int_0^1 e^{-\tau[(\kappa-1)t+1]} B_n(\tau t) t^{n+\ell+1} dt$$

* See Page 224, Ref. [30].

$$(3.16) \quad \overline{G}_{n\ell}^s = \tau^{\ell+1} \int_1^{\infty} e^{-\tau[(\kappa+1)t-1]} C_n(\tau t) t^{\ell-n} dt .$$

The B_n functions, which also appear in the $C_{\alpha\beta}^{\gamma\delta\epsilon}$ - functions, are calculated by the formulas

$$(3.17) \quad \begin{aligned} B_{-1} &= e^{-z} \cosh z \\ B_0 &= z^{-1} e^{-z} \sinh z \\ B_n &= (4n^2-1) z^{-2} (B_{n-2} - B_{n-1}) . \end{aligned}$$

For low values of z , the forward recurrence procedure loses accuracy. Therefore, for z below a certain criterion, the backward recurrence procedure, starting at high n with $B'_n = B'_{n+1}$ equal to an arbitrary number, is applied, giving a series B'_{n+1}, \dots, B'_{-1} . Then the correct values of the B_n functions are obtained by multiplying the whole series by B_{-1}/B'_{-1} where B_{-1} is calculated, without differencing errors, from the first equation in (3.17).

The recurrence scheme for the C_n functions is

$$(3.18) \quad \begin{aligned} C_{-1} &= z^{-1} \\ C_0 &= 1 \\ C_{n+1} &= (2n+3)^{-1} \{ (2n+1)C_n + z^2(2n+1)^{-1}C_{n-1} \} . \end{aligned}$$

This procedure is accurate for increasing n and all $z \geq 0$.

The $\bar{G}_{n\ell}^i$ functions lose accuracy rapidly when recurrence relations in n and ℓ are applied, so these are calculated by Legendre-Gauss numerical integration.

For the $\bar{G}_{n\ell}^s$ functions, recurrence methods work quite well, so the following procedure was devised for their calculations:

First, the functions with $n = 0$ are

$$(3.19) \quad \bar{G}_{0\ell}^s = e^\tau \tau^{\ell+1} \int_1^\infty e^{-\tau(\kappa+1)t} t^\ell dt.$$

By partial integration, the recurrence relation

$$(3.20) \quad \bar{G}_{0\ell}^s = (\kappa+1)^{-1} \{ \tau^\ell e^{-\kappa\tau} + \ell \bar{G}_{0,\ell-1}^s \}$$

is obtained. This and the starting function

$$(3.21) \quad \bar{G}_{00}^s = (\kappa+1)^{-1} e^{-\kappa\tau}$$

give $\bar{G}_{0\ell}^s$ for all $\ell \geq 0$. For $\ell < 0$, (3.20) is used to decrease ℓ , starting with

$$(3.22) \quad \bar{G}_{0,-1}^s = e^{-\kappa\tau} \{ -e^{\tau(\kappa+1)} \text{Ei}(-\tau(\kappa+1)) \}$$

where

$$(3.23) \quad \text{Ei}(z) = - \int_1^\infty t^{-1} e^{zt} dt$$

is the familiar exponential integral. By the form of \bar{G}_{nl}^s in (3.16) and the definition of C_{-1} and C_0 in (3.18), it is seen that

$$(3.24) \quad \bar{G}_{-1,l}^s = \bar{G}_{0,l}^s \tau^{-1}.$$

The above procedure provides all the necessary \bar{G}_{nl}^s 's with $n = -1$ and 0 . For higher values of n , the relation

$$(3.25) \quad \bar{G}_{nl}^s = (2n+1)^{-1} \left\{ \tau(2n-1) \bar{G}_{n-1,l-1}^s + \tau^2(2n-1)^{-1} \bar{G}_{n-2,l}^s \right\}$$

is used. Equation (3.25), which is derived by substituting (3.18) in (3.16), does not lose accuracy as n is increased.

4. Tables of Integrals

Tables T I, T II, T III can be used to obtain numerical values of the one-electron integrals (1.4) - (1.9), most, but not all, of the electric field gradient integrals (1.10), and the two-electron Coulomb (1.13) and Hybrid (1.14) integrals. The range of parameters is such that one can, by interpolation, obtain approximately six significant figures in the integrals required for the calculation of the first row diatomic molecules for a range of R at least up to their dissociation distances.

The integrals in T I can be used with the simple formulas given there to obtain the overlap, kinetic energy, and nuclear attraction integrals. With the exception already mentioned above, the integrals (1.4) - (1.10) can also be obtained in terms of the $C_{\alpha\beta}^{\gamma\delta\epsilon}$ functions of T III. Explicit expressions for these and a number of other one-electron integrals in terms of the $C_{\alpha\beta}^{\gamma\delta\epsilon}$ functions can easily be written by referring to the definition (2.1) of the $C_{\alpha\beta}^{\gamma\delta\epsilon}$ functions.

Aside from a simple multiplicative factor, two-electron Coulomb integrals of the real STO's are given directly in T II as functions of p and t (see Equation (2.2)). All Coulomb integrals for the real or complex STO's defined above can be expressed as simple linear combinations of the integrals in the tables. To calculate these integrals, formulas for them in terms of $C_{\alpha\beta}^{\gamma\delta\epsilon}$ functions with $\alpha \geq 0$ were derived by the method described in Sections 1 and 2. In deriving formulas for the Coulomb integrals, one can perform the first integration over the coordinates of either electron 1 or 2. Thus, one can form two different expressions for each non-symmetric Coulomb integral. The values of the argument t in the two formulas are opposite in sign and, in general, the expression having $t < 0$ is subject to differencing effects. Therefore, two expressions for each Coulomb integral were programmed and, in all cases, the one

with $t \geq 0$ was used. The tabulation of the Hybrid integrals is more complicated since they are functions of three parameters even after a multiplicative factor is taken out. Therefore, tables of the two-parameter $C_{\alpha\beta}^{\gamma\delta\epsilon}$ functions in T III were constructed for their calculation. The user is then required to obtain appropriate $C_{\alpha\beta}^{\gamma\delta\epsilon}$ functions from the table and form linear combinations of them for each Hybrid integral.

As mentioned previously, the analytic expressions for $C_{\alpha\beta}^{\gamma\delta\epsilon}$, $\alpha < 0$, provided by Roothaan, do not give accurate results in the range of parameters where pt is small. Therefore, this procedure was used for pt large, where accurate results could be obtained, and the slower Zeta-function method (Section 3 above) was used to calculate the $C_{\alpha\beta}^{\gamma\delta\epsilon}$'s for the rest of the table. Fortunately, the latter method is faster and more accurate in precisely the regions of the table where the former gives errors. There were large regions of each table of $C_{\alpha\beta}^{\gamma\delta\epsilon}$ functions where both methods gave the same results.

After the tables were finished, the programs used in their calculation were converted into subroutines which are capable of producing all of the integrals (1.4) - (1.10). For a given set of parameters, these integrals can be calculated in a few seconds. The programs for the calculations reported below used these subroutines for all the integrals involved.

IV A NUMERICAL METHOD FOR SOLVING THE RADIAL SCHROEDINGER EQUATION

1. Introduction

The wave equation for the nuclear motion of a diatomic molecule, in the Born-Oppenheimer approximation, is one which is encountered frequently in quantum theoretical calculations. Numerical methods for its solution have been developed and used [4,31,32,33] over many years for atomic problems where the potential is one obtained by Hartree-Fock self-consistent fields or the Thomas-Fermi-Dirac statistical field methods. Only relatively recently have computational techniques and the application of electronic computers enabled one to obtain accurate theoretical internuclear potentials at enough internuclear distances to calculate the wave functions for the motion of the nuclei and use them to obtain averages, over nuclear motion, of molecular properties.

The present investigation is concerned with obtaining an accurate method for calculating the nuclear wave functions and vibrational-rotational energies of diatomic molecules with some economy in the number of values of the internuclear potential required. In this chapter, an improved formula for the correction of trial eigenvalues, which does not depend so much for its accuracy upon the smallness of the step-size in the radial coordinate, and an analysis of the

convergence of the procedure are given. A computer sub-routine was written and numerical results obtained from it are given for a case where exact analytic solutions are known.

In what follows, the vibrational quantum number v , $v = 0, 1, 2, \dots$, will be used as a subscript to index the eigenvalues E_v with the usual convention that $E_0 \leq E_1 \leq E_2 \leq \dots$.

2. Method of Integration.

The Schrodinger wave equation for the motion of the nuclei of a diatomic molecule, regarded as a symmetric top, can be expressed in polar spherical coordinates R, Θ, Φ of one nucleus relative to the other and one additional coordinate, ϕ , giving the angular orientation of the electronic charge cloud about the internuclear axis. It has been shown [34] that the wave equation can be separated into its angular and radial parts and its solution may be expressed in the form

$$\Psi = R^{-1} P(R) Y_{JM}(\Theta, \Phi, \phi)$$

where $P(R)$ is the solution of the one-dimensional radial Schrodinger equation

$$\begin{aligned} (2.1) \quad P^{(2)}(R) &= (U(R) - E) P(R), \\ P^{(n)}(R) &= d^n P(R) / dR^n, \end{aligned}$$

the $Y_{J\Lambda M}$'s are the hypergeometric functions, Λ is the z-component of electronic angular momentum, and the radial internuclear potential, $U(R)$, is of the form

$$U(R) = [J(J+1) - \Lambda^2] R^{-2} + Z_a Z_b R^{-1} + E_{el}(R) .$$

The second term is the electrostatic Coulomb repulsion energy of the nuclei and $E_{el}(R)$ is the electronic energy obtained by solving the electronic wave equation discussed in Chapter II. The boundary conditions for (2.1) are:

$$P(0) = 0, \quad P(R) \text{ bounded.}$$

To get a difference equation whose solutions approximate the solutions of (2.1) we let

$$\begin{aligned} (2.2) \quad R_i &= ih, & i &= 0, 1, 2, \dots, n+1, \\ P_i &= P(R_i), \\ U_i &= U(R_i). \end{aligned}$$

By dropping terms of the fourth order and higher in the series

$$(2.3) \quad P_{i+1} + P_{i-1} = \sum_{k=0}^{\infty} \frac{2h^{2k}}{(2k)!} P_i^{(2k)}$$

and using the differential equation to replace $P_i^{(2k)}$, one obtains the simple integration formula

$$(2.4) \quad P_{i+1} + P_{i-1} - 2P_i = h^2(U_i - E)P_i$$

which has an error of approximately $\frac{h^4}{12} P_i^{(4)}$. A higher

order integration formula, which does not involve any more values of P_i , can be obtained by subtracting $h^2/12$ times the series

$$(2.5) \quad P_{i+1}^{(2)} + P_{i-1}^{(2)} = \sum_{k=0}^{\infty} \frac{2h^{2k}}{(2k)!} P_i^{(2k+2)}$$

from (2.3). Then, dropping sixth and higher order terms in h gives

$$(2.6) \quad Y_{i+1} + Y_{i-1} - 2Y_i = h^2(U_i - E)P_i$$

where

$$(2.7) \quad Y_i = P_i - \frac{h^2}{12} P_i^{(2)} = [1 - \frac{h^2}{12} (U_i - E)] P_i.$$

The error in (2.6) is approximately $-\frac{h^6}{240} P_i^{(6)}$. The integration formula (2.6), usually attributed to Numerov [35], involves the extra calculation of the Y_i 's but reduces the number of points where values of $U(R)$ are required.

In the range $E \geq U(\infty)$, corresponding to unbound states of the two nuclei, solutions of (2.1) exist for all E and can be approximated by simply using (2.4) or (2.6) to integrate outward, starting with the boundary values,

$$(2.8) \quad P_0 = 0, \quad P_1 = \text{a small arbitrary number.}$$

For $E < U(\infty)$, the two nuclei are bound together and solutions of (2.1) exist only for a set of discrete

values of E , the eigenvalues of the problem. The method for calculating these eigenvalues and corresponding solutions, or eigenfunctions, is the subject of the present chapter.

The boundary condition, $P(R)$ bounded, is approximated, as usual, by the conditions

$$\begin{aligned} P_{n+1} &= \text{a small arbitrary number} \\ (2.9) \quad P_n &= P_{n+1} \exp(R_{n+1} \sqrt{U_{n+1}-E} - R_n \sqrt{U_n-E}) . \end{aligned}$$

The second of these conditions results from the assumption that, at R_n , $U(R)$ is slowly approaching a constant.

The usual numerical procedure is to provide a first estimate of E and integrate outward from $R = 0$ to some point R_m using starting values (2.8) and integration formula (2.4) or (2.6). Since (2.1) is homogeneous in $P(R)$, the resulting P_i values may be replaced by $P_i^{\text{out}} = P_i/P_m$, $i = 1, 2, \dots, m$. With starting values (2.9), the same procedure is used to integrate inward from R_{n-1} to R_m and yields values P_i^{in} , $i = n-1, n, \dots, m$ such that $P_m^{\text{in}} = P_m^{\text{out}} = 1$. Then, a correction to E is determined by the difference between the slopes of the two curves at the crossing-point R_m and the process is repeated until the two curves meet with the same derivative. The correction $D(E)$ is usually* calculated by

* See Equation 6, page 86, of Ref. [4].

using the formula

$$(2.10) \quad D(E) = (P'_{\text{out}} - P'_{\text{in}}) / \int_0^{\infty} P(R) dR$$

where the terms in the numerator are the derivatives at R_m of the curves resulting from the outward and inward integration, respectively.

Equation (2.10) has been derived from the differential equation and is claimed to give first order convergence in the error. This means that if a trial solution satisfies the differential equation (2.1) at all points except R_m , then (2.10) deviates from the true correction by an amount which is proportional to the correction. In the next section, it will be shown that the eigenvalues of the difference equations, (2.4) or (2.6) are the zeroes of appropriate functions of the trial eigenvalue E and that these zeroes can conveniently be calculated by the Newton-Raphson method. The correction is

$$(2.11) \quad D(E) = -F(E)/F'(E)$$

where $F(E)$ is a function whose form depends upon the integration formula used. For E near an eigenvalue E_0 ,

$$(2.12) \quad D(E) = \Delta E + (\Delta E)^2 Q + \text{higher order terms in } \Delta E$$

where $\Delta E = E_0 - E$ and

$$(2.13) \quad Q = F''(E_0)/2F'(E_0) \quad .$$

Thus, the convergence of the present method is of second order in $\triangle E$. In Section 4, an analysis of the behavior of $D(E)$ over the whole range of E is given.

3. Correction Formula.

The integration formulas (2.4) and (2.6) can be written as systems of equations in the P_i 's and Y_i 's respectively, as follows:

$$\begin{aligned}
 (2h^{-2} + U_1 - E)P_1 - h^{-2}P_2 &= 0 \\
 (3.1) \quad -h^{-2}P_{i-1} + (2h^{-2} + U_i - E)P_i - h^{-2}P_{i+1} &= 0 \\
 -h^{-2}P_{n-1} + (h^{-2} + U_n - E)P_n &= 0
 \end{aligned}$$

and

$$\begin{aligned}
 \{2h^{-2} + (U_1 - E)[1 - \frac{h^2}{12}(U_1 - E)]^{-1}\}Y_1 - h^2Y_2 &= 0 \\
 (3.2) \quad -h^{-2}Y_{i-1} + \{2h^{-2} + (U_i - E)[1 - \frac{h^2}{12}(U_i - E)]^{-1}\}Y_i - h^2Y_{i+1} &= 0 \\
 -h^{-2}Y_{n-1} + \{h^{-2} + (U_n - E)[1 - \frac{h^2}{12}(U_n - E)]^{-1}\}Y_n &= 0
 \end{aligned}$$

where $i = 2, 3, \dots, n-1$ in both cases. A term involving E has been omitted from the n -th equation in both (3.1) and (3.2). It can easily be shown that if one has, as one should, started the inward integration at a large enough R_n to justify the assumption used in forming the boundary condition (2.9), this omission is justified.

The procedure used here to derive and analyze the

correction formula is an adaptation of a very general and effective technique, due to Löwdin [36], for calculating solutions of the Schroedinger equation. To apply Löwdin's method, consider the vector-matrix formulation of equations (3.1) or (3.2),

$$(3.3) \quad \underline{M} \underline{C} = \underline{0} ,$$

where $\underline{0}$ is a null-vector, \underline{C} is a vector containing the P_i 's or the Y_i 's, and \underline{M} is the symmetric matrix of coefficients which, for the present, may simply be regarded as functions of E . After an outward and an inward integration with a trial value of E , all equations except the m -th are satisfied. Now, assume that the first row of \underline{M} and the first element of \underline{C} correspond to the m -th equation and the m -th variable, respectively, in equations (3.1) or (3.2). Then, by partitioning the first index of \underline{M} and \underline{C} , the result of the integration can be expressed

$$(3.4) \quad \begin{pmatrix} M_{11} & M_{a1}^+ \\ M_{a1} & M_{aa} \end{pmatrix} \begin{pmatrix} 1 \\ \underline{C}_a \end{pmatrix} = \begin{pmatrix} F(E) \\ \underline{0} \end{pmatrix}$$

where $F(E)$ is the amount by which the m -th equation of (3.1) or (3.2) is not satisfied when integrating with the trial value E . It is assumed that the first element of \underline{C} , which is P_m or Y_m , is non-zero and, for convenience,

it is set equal to 1. Equation (3.4) may be written in the form

$$(3.5) \quad F(E) = M_{11} + \underline{M}_{a1}^+ \underline{C}_a$$

$$(3.6) \quad \underline{0} = \underline{M}_{a1} + \underline{M}_{aa} \underline{C}_a .$$

The function $F(E)$, whose zeros are the eigenvalues of the difference equations, is defined by (3.5) in terms of \underline{C}_a which, in turn, is defined as a solution of (3.6). Furthermore, if E is such that $|\underline{M}_{aa}| \neq 0$, then the solution of (3.6) is unique and $F(E)$ is uniquely defined. An expression for $F'(E)$ is obtained by differentiating (3.5) and (3.6) with respect to E and obtaining

$$(3.7) \quad F'(E) = M'_{11} + \underline{M}_{a1}'^+ \underline{C}_a + \underline{M}_{a1}^+ \underline{C}_a'$$

$$(3.8) \quad \underline{0} = \underline{M}_{a1}' + \underline{M}_{aa}' \underline{C}_a + \underline{M}_{aa} \underline{C}_a' .$$

Multiplying (3.8) on the left by \underline{C}_a^+ gives

$$(3.9) \quad \underline{0} = \underline{C}_a^+ \underline{M}_{a1}' + \underline{C}_a^+ \underline{M}_{aa}' \underline{C}_a + \underline{C}_a^+ \underline{M}_{aa} \underline{C}_a' .$$

From (3.6) it is seen that if (3.7) and (3.9) are added, the terms containing \underline{C}_a' cancel and the result is

$$(3.10) \quad F'(E) = M'_{11} + \underline{M}_{a1}'^+ \underline{C}_a + \underline{C}_a^+ \underline{M}_{a1}' + \underline{C}_a^+ \underline{M}_{aa}' \underline{C}_a$$

which can be written

$$(3.11) \quad F'(E) = \underline{C}^+ \underline{M}' \underline{C} .$$

In the two cases considered here, only diagonal elements of \underline{M} depend upon E so that the correction formula (2.11) can be written

$$(3.12) \quad D(E) = -F(E) / \sum_{i=1}^n c_i^2 M'_{ii} .$$

In the case of (3.1), the derivatives of the diagonal elements of \underline{M} are all equal to -1 so (3.12) becomes

$$(3.13) \quad D(E) = [(-P_{m-1} + 2P_m - P_{m+1})h^{-2} + (U_m - E)P_m] / \sum_{i=1}^n P_i^2 .$$

It is of some interest to compare this with the correction formula (2.10). If, in (2.10), central differences at R_m are used to estimate the derivatives and the trapezoidal rule is used to estimate the integral in the denominator, then (2.10) is the same as (3.13). Therefore, use of the integration formula (3.1) and correction formula (2.10) as described above yields a second order process in ΔE .

In the case of the Numerov integration formula, where equations (3.2) are solved, the derivatives of the diagonal elements of \underline{M} are

$$(3.14) \quad M'_{ii} = -[1 - \frac{h^2}{12} (U_i - E)]^{-2} , \quad i = 1, 2, \dots, n.$$

By substituting P_i 's for Y_i 's the correction formula (3.12) becomes

$$(3.15) \quad D(E) = [(-Y_{m-1} + 2Y_m - Y_{m+1})h^{-2} + (U_m - E)P_m] / \sum_{i=1}^n P_i^2.$$

4. Convergence.

A rigorous treatment of the convergence of the method, when the Numerov integration formula (3.2) is used, would be quite complicated. Furthermore, since the difference in the two methods considered is a term of order h^4 in the solution $P(R)$ and since both are second order processes in ΔE , one is justified in assuming that the essential features of the convergence of the two procedures will be about the same. Therefore, the convergence of the method using equations (3.1) will be considered here.

To get expressions for $F(E)$, $F'(E)$, and $D(E)$, let

$$(4.1) \quad \underline{H} = \begin{pmatrix} G_m & & & & & & & & & \\ & K & & & & & & & & \\ & & G_1 & & & & & & & \\ & & & K & & & & & & \\ & & & & K & & & & & \\ & & & & & K & & & & \\ & & & & & & G_{m-1} & & & \\ & & & & & & & K & & \\ & & & & & & & & G_{m+1} & \\ & & & & & & & & & K \\ & & & & & & & & & & K \\ & & & & & & & & & & & G_n \end{pmatrix}$$

where

$$\begin{aligned}
 K &= -h^{-2} \ , \\
 G_i &= 2h^{-2} + U_i \ , \quad i = 1, 2, \dots, n-1, \\
 G_n &= h^{-2} + U_n \ ,
 \end{aligned}$$

and where the blank spaces denote zero elements.

Then, for equations (3.1),

$$(4.2) \quad \underline{M} = \underline{H} - \underline{1} E$$

where $\underline{1}$ is the identity matrix. The symmetric matrix \underline{M}_{aa} can be diagonalized by an orthonormal matrix \underline{U} , whose columns are the eigenvectors of both \underline{M}_{aa} and \underline{H}_{aa} . Thus,

$$(4.3) \quad \underline{M}_{aa} = \underline{U} \underline{\Lambda} \underline{U}^+$$

where $\underline{\Lambda}$ is a diagonal matrix with the eigenvalues of \underline{M}_{aa} on its diagonal. Then, if no eigenvalue of \underline{M}_{aa} is zero, a solution of (3.6) exists and can be written

$$(4.4) \quad \underline{C}_a = -\underline{M}_{aa}^{-1} \underline{M}_{a1} = -\underline{U} \underline{\Lambda}^{-1} \underline{U}^+ \underline{M}_{a1} \ .$$

Letting

$$(4.5) \quad \underline{V} = \underline{U}^+ \underline{M}_{a1}$$

and substituting (4.4) for \underline{C}_a in (3.5), one obtains

$$\begin{aligned}
 (4.6) \quad F(E) &= \underline{M}_{11} - \underline{V}^+ \underline{\Lambda}^{-1} \underline{V} \ . \\
 &= \underline{M}_{11} - \sum_v \underline{V}_v^2 \lambda_v^{-1} \ .
 \end{aligned}$$

As one can see from (4.2), the diagonal elements of $\underline{\Lambda}$ are

$$(4.7) \quad \lambda_v = e_v - E$$

where e_v , $v = 1, 2, \dots, n-1$, $e_v \leq e_{v+1}$, are the eigenvalues of \underline{H}_{aa} , the matrix obtained by deleting the first row and column of \underline{H} . Hence,

$$(4.8) \quad F(E) = 2h^{-2} + U_m - E - \sum_v v_v^2 (e_v - E)^{-1}$$

and

$$(4.9) \quad F'(E) = -1 - \sum_v v_v^2 (e_v - E)^{-2}.$$

The set of points R_1, \dots, R_{m-1} , R_{m+1}, \dots, R_n , referred to by the subscript "a" in the vectors and matrices above, may be partitioned into the set of points R_1, \dots, R_{m-1} , used in the outward integration, and the set of points R_{m+1}, \dots, R_n used in the inward integration. Letting "out" and "in" subscripts denote the subvectors and submatrices resulting from this partitioning, \underline{H}_{aa} can be written

$$(4.10) \quad \underline{H}_{aa} = \begin{pmatrix} \underline{H}_{out} & \underline{0} \\ \underline{0} & \underline{H}_{in} \end{pmatrix}$$

where \underline{H}_{out} and \underline{H}_{in} are the block matrices lying on the diagonal in (4.1) and enclosed by the dashed lines. By

partitioning in this manner, (4.3) can be written

$$\underline{M}_{out} = \underline{U}_{out} \underline{\Lambda}_{out} \underline{U}_{out}^+ \quad (4.11)$$

$$\underline{M}_{in} = \underline{U}_{in} \underline{\Lambda}_{in} \underline{U}_{in}^+$$

where the columns of \underline{U}_{out} and \underline{U}_{in} are the eigenvectors of \underline{H}_{out} and \underline{H}_{in} respectively. Therefore, e_v , $v = 1, 2, \dots, n-1$, are the eigenvalues of \underline{H}_{out} and \underline{H}_{in} . From the form of \underline{H} , it is evident that these are the solutions which, on the outward and inward integrations, respectively, lead to $P_m = 0$ which is contrary to the assumption that the first element of \underline{C} is nonzero.

To show that $F(E)$ is undefined at and only at the eigenvalues e_v it is necessary to show that no V_v is zero in (4.8). This is evident since (4.5) and the form of \underline{M}_{al} imply that the elements of \underline{V} are $-h^{-2}$ times the elements in the last row of \underline{U}_{out} and the first row of \underline{U}_{in} . If any such element of \underline{U}_{out} or \underline{U}_{in} were zero, then, since \underline{M}_{out} and \underline{M}_{in} are tridiagonal matrices, the column containing that element would be zero. This, of course, is not so, since these columns are the eigenvectors of \underline{M}_{out} and \underline{M}_{in} .

It may be of some interest to show how the characteristic polynomial,

$$(4.12) \quad P(E) = |\underline{M}| ,$$

of (3.1) is related to $F(E)$. From (4.3) and (4.5), one gets

$$(4.13) \quad P(E) = \begin{vmatrix} M_{11} & \underline{V}^+ \\ \underline{V} & \underline{\Lambda} \end{vmatrix}$$

which can be expanded in the elements of the first row and column of the determinant to give

$$(4.14) \quad \begin{aligned} P(E) &= M_{11} \prod_{v'} \lambda_{v'} - \sum_v V_v^2 \prod_{v' \neq v} \lambda_{v'} \\ &= (M_{11} - \sum_v V_v^2 \lambda_v^{-1}) \prod_v \lambda_v \end{aligned}$$

From (4.6) and (4.7),

$$(4.15) \quad P(E) = F(E) \prod_v (e_v - E) .$$

Equations (4.8) and (4.9) enable one to determine the general behavior of $F(E)$ and $D(E)$. They show, first of all, that $F(E)$, $F'(E)$, and $D(E)$ are defined and continuous for all E except $E = e_v$, $v = 1, 2, \dots, n-1$ and that

$$\begin{aligned}
(4.16) \quad & F(E) \approx 2h^{-2} + U_m - E && \text{for } |E| \text{ large,} \\
& F(E) < 2h^{-2} + U_m - E && \text{for } E < e_1, \\
& F(E) > 2h^{-2} + U_m - E && \text{for } E > e_{n-1}, \\
& F(E) \approx -V_v^2(e_v - E)^{-1} && \text{for } E \approx e_v, \\
& F'(E) < -1 && \text{for all } E, \\
& F'(E) \approx -1 && \text{for } |E| \text{ large,} \\
& F'(E) \approx -V_v^2(e_v - E)^{-2} && \text{for } E \approx e_v.
\end{aligned}$$

Therefore, in each of the intervals into which the points e_v divide the E -axis, $F(E)$ is a continuous decreasing function which goes from positive to negative values.

Hence, in each such interval, $F(E)$ must have one and only one zero. Let these zeros be denoted E_v , $v = 0, 1, 2, \dots, n-1$, with $E_0 < e_1$, $e_v < E_v < e_{v+1}$, $e_{n-1} < E_{n-1}$. The index v is, therefore, the vibrational quantum number. From (4.16), it is seen that the correction formula (3.13) has the following properties:

$$\begin{aligned}
(4.17) \quad & D(E) \approx E - e_v && \text{for } E \approx e_v, \\
& D(E) \approx 2h^{-2} + U_m - E && \text{for } |E| \text{ large,} \\
& D(E) < 2h^{-2} + U_m - E && \text{for } E < e_1, \\
& D(E) > 2h^{-2} + U_m - E && \text{for } E > e_{n-1}, \\
& D(E) \approx E_v - E && \text{for } E \approx E_v.
\end{aligned}$$

The last condition is a general property of the Newton-Raphson method (see (2.12)). A plot of $F(E)$ and $D(E)$,

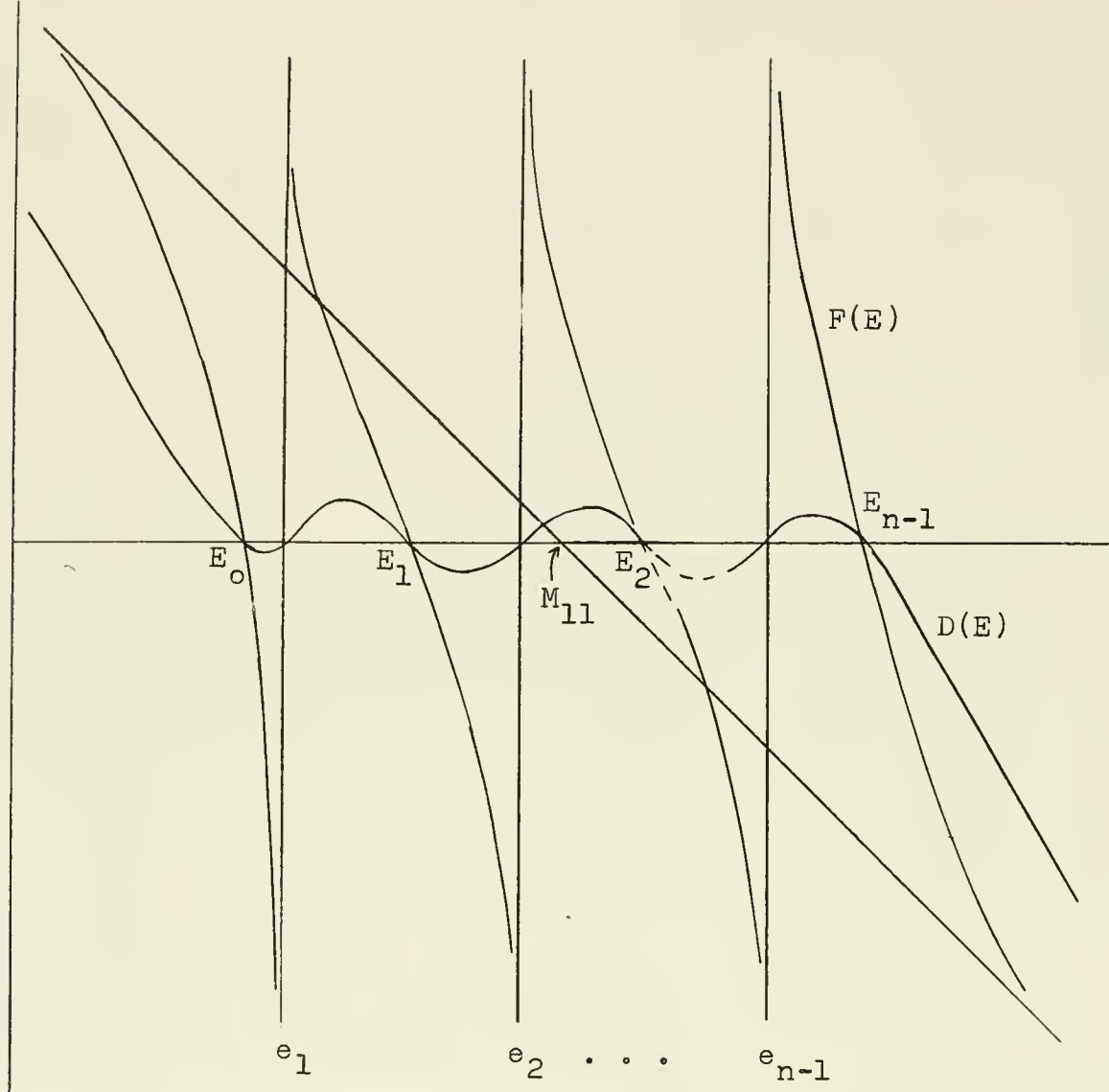


Fig. 2. Behavior of $F(E)$ and $D(E)$ Curves

derived from the above analysis, may be expected to appear as shown in Figure 2.

A serious convergence difficulty is immediately obvious from the first property of $D(E)$. This indicates not only that $E \approx e_v$ leads to a gross underestimate of the correction for such values of E , but that the smallness of $D(E)$ cannot, by itself, be used as a convergence criterion. The condition $E \approx e_v$ can easily be detected by the existence of a large $F'(E)$ and an increase in $D(E)$ from one iteration to the next. Another difficulty which may occur is a jumping from one branch of the $F(E)$ curve to another on successive iterations. This can cause one to miss some desired eigenvalues and waste computing effort in converging to eigenvalues which are not wanted or which have already been computed. Convergence problems, therefore, are related to the distribution of the vertical asymptotes at e_v , which are determined by the crossing point R_m , and to the selection of initial trial values of E .

To investigate the role of R_m , consider the convergence factor (2.13),

$$(4.18) \quad Q = F''(E_v) / 2F'(E_v) ,$$

of the Newton-Raphson method. For $E_v \approx e_v$,

$$(4.19) \quad Q \approx (e_{v1} - E_v)^{-1} ,$$

showing that Q is large and convergence is poor if an eigenvalue E_v is near a vertical asymptote. It was pointed out above that e_v is a value of E for which $P_m = 0$ on the inward or outward integration. Therefore, $E_v \approx e_v$, is the situation where, for the correct solution, $P_m \approx 0$. In other words, convergence is poor if R_m is near a node of the desired solution. Some practical means for selecting the crossing-point, R_m , and the initial estimates of E are given in the next section.

5. Application.

A computer subroutine was written which, when given a numerical potential, an initial estimate of E , and an ϵ , integrates by the Numerov method (Equation (2.6)) and uses (3.15) to correct E . After $D(E)$ starts decreasing from one iteration to the next, the convergence criterion $D(E) \leq \epsilon$ is applied.

In order to keep R_m as far as possible from a node of the solution and to acquire maximum significance where the solution is large, R_m is selected during the integration as the point where $|P_i|$ is largest. Since, for the applications considered, this occurs at the outermost maximum point of $|P_i|$, the inward integration is performed first and R_m is taken as the point at which $|P_i|$ stops increasing with decreasing i . The description of the

behavior of $F(E)$, given in the previous section, is somewhat invalidated since, there, it was assumed that R_m was held fixed while varying E . Instead, the $F(E)$ given by the present program will behave like $F(E)$ of the previous section in each interval where the variation of E does not change R_m .

The data used here to demonstrate the method was obtained for the case where $U(R)$ of equation (2.1) is a Morse potential* [37]

$$U(R) = D [1 - \exp(-a(R-R_e))]^2 - D.$$

Values of the correct analytic solution are given for comparison. The range $0 \leq R \leq 10$ was used in all cases. A graph of the calculated $D(E)$ is given in Figure 3 for E in the region of the two lowest eigenvalues. The effect of the shifting R_m is evident. As one might expect, the discontinuities are large in the region of the e_v 's, where the solution curves cross with large slopes. On the other hand, there is a large region about each eigenvalue E_v where such discontinuities are negligible and where $D(E)$ is almost a straight line of

* The parameters used are: $a = .711248$, $R_e = 1.9975$, $D = 188.4355$. These were obtained by fitting the Morse potential to a computed potential curve for H_2^+ . Energies are given in units of 2μ a.u. where μ is the reduced mass of the nuclei.

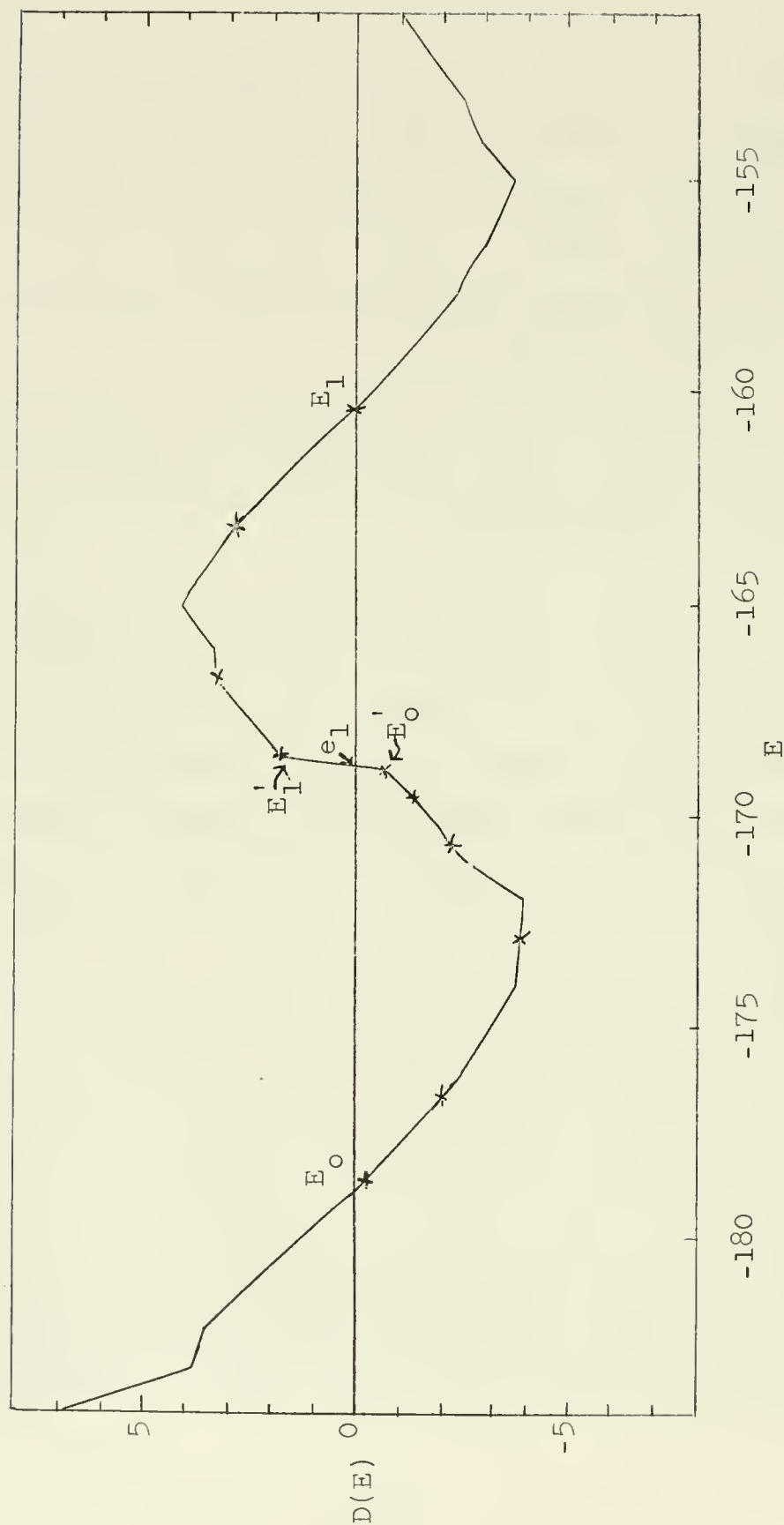


Fig. 3. Graph of Calculated $D(E)$.

Crosses on curve denote successive iterations obtained with poor starting values E_0 and E_1 .

slope -1 and is, therefore, a good estimate of the necessary correction.

To show how the procedure converges when a poor first estimate of E is used, the program was given a value of E near e_1 . As one can see in Table 2, where the successive trial values are given, and in Figure 3, $D(E)$ increases for a number of iterations and then goes down rapidly. Table 3 gives some of the eigenvalues obtained for $n = 50, 100, 150$, and 200 points. Exact values of the analytic solution are given for comparison. Table 4 contains some of the values of the $v = 0$ eigenfunctions which were obtained with $50, 100$, and 200 points. Values obtained from the exact solution are given in the last column. Figure 4 contains a graph of the potential (5.1) and the wave functions obtained for the $v = 0, 1$, and 2 states.

TABLE 2. SUCCESSIVE ITERATES OBTAINED WITH POOR FIRST
ESTIMATES OF E_0 AND E_1

i	$E_0^{(i)}$	$F(E_0^{(i)})$	$E_1^{(i)}$	$F(E_1^{(i)})$
1	-168.800 00	-1470.	-168.500 00	456.7
2	-169.450 37	-727.9	-166.581 98	220.5
3	-170.700 20	-350.7	-163.292 37	58.21
4	-172.904 49	-113.0	-160.385 38	1.654
5	-176.702 14	-26.24	-160.283 89	.0003
6	-178.624 20	-2.042	-160.283 69	$.1550 \times 10^{-4}$
7	-178.797 03	$-.1786 \times 10^{-1}$		
8	-178.798 56	$-.5185 \times 10^{-4}$		
9	-178.798 57	$-.1228 \times 10^{-5}$		

TABLE 3. DEPENDENCE OF EIGENVALUES ON n , THE NUMBER
OF INTEGRATION POINTS

n	E_0	E_1	E_2	E_3	E_4
50	-178.81052	-160.35850	-143.02050	-126.83300	-111.81094
100	-178.79924	-160.28784	-142.79397	-126.31918	-110.86348
150	-178.79866	-160.28428	-142.78276	-126.29441	-110.81921
200	-178.79857	-160.28368	-142.78090	-126.29031	-110.81191
Exact	-178.79850	-160.28182	-142.77990	-126.28824	-110.80832

TABLE 4. DEPENDENCE OF WAVE FUNCTION $P(R)$, FOR $v = 0$,
ON n , THE NUMBER OF INTEGRATION POINTS

R	P(R)			
	n = 50	n = 100	n = 200	Exact
1.2	.022 5903	.022 3875	.022 3754	.022 3746
1.6	.484 0974	.485 8844	.485 9864	.485 9927
2.0	1.312 2858	1.310 2630	1.310 1471	1.310 1405
2.4	.732 9700	.734 7376	.734 8413	.734 8476
2.8	.126 3448	.126 4907	.126 4998	.126 5004
3.2	.008 9574	.008 9544	.008 9541	.008 9541

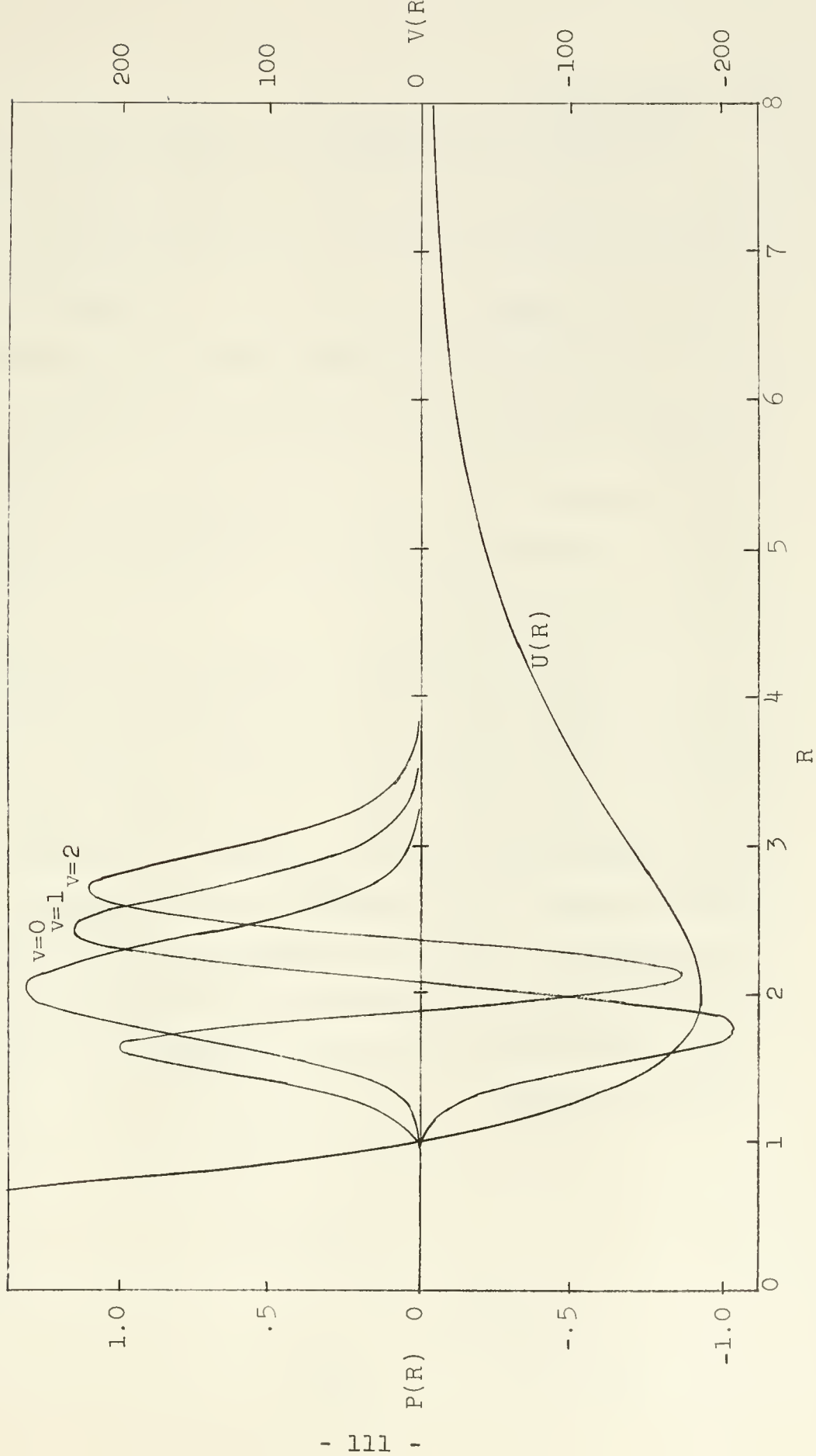


Fig. 4. Plot of Potential $U(R)$ and $v = 0, 1, 2$ Solutions

6. Conclusions.

The above results indicate that fairly good accuracy can be achieved rapidly by the above procedure, but that good first trial values are quite important, not only in reducing the number of iterations, but in assuring that no desired solutions are missed. Good first estimates of E_v can be obtained by fitting an analytic potential for which eigenvalues are known and using it to obtain first estimates of the lowest eigenvalues. An extrapolation of calculated eigenvalues can then give an approximation to each new eigenvalue.

If it is inconvenient to obtain first estimates of E in this manner, one can have the computer subroutine perform just one iteration for each of a series of values of E to get a $D(E)$ curve. Then, in each interval where $D(E)$ changes from positive to negative, there is an eigenvalue for which a first estimate can be obtained by interpolation of $D(E)$. A count of the nodes in the solution, given by the subroutine, is a check on the vibrational quantum number assigned and assures that no desired solution is missed.

V THE EVALUATION OF MOLECULAR PROPERTIES

1. The Calculation of Energy Levels and Band Spectrum Constants.

In the Born-Oppenheimer approximation, the energy levels of the diatomic molecule in an electronic Σ -state are taken as the eigenvalues of the radial Schroedinger equation

$$(1.1) \quad d^2S(R)/dR^2 = 2\mu(U(R) - E) S(R)$$

where

$$(1.2) \quad U(R) = J(J+1)/2\mu R^2 + V(R)$$

$$(1.3) \quad V(R) = Z_a Z_b R^{-1} + E_{el}(R) .$$

The integer J is the rotational quantum number, μ is the reduced mass of the nuclei, $Z_a Z_b R^{-1}$ is the ordinary Coulomb repulsion energy of the nuclei, and $E_{el}(R)$ is the electronic energy. It is assumed for convenience that $V(\infty) = 0$. In the usual terminology, the equilibrium distance R_e , the binding energy D , and the force constant γ are defined in terms of (1.3) by

$$(1.4) \quad \begin{aligned} [dV/dR]_{R=R_e} &= 0 \\ D &= -V(R_e) \\ \gamma &= [d^2V/dR^2]_{R=R_e} \end{aligned}$$

Morse [37] has constructed the hypothetical inter-nuclear potential function

$$(1.5) \quad V_M(R) = D[1 - e^{-a(R-R_e)}]^2 - D$$

where

$$(1.6) \quad a = \sqrt{\gamma/2D} \quad .$$

If $V_M(R)$ is substituted for $V(R)$ in (1.2), the resulting energy levels, or term values, are given [38] by

$$(1.7) \quad \begin{aligned} T_{vJ} = & -D + \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + B_e J(J+1) \\ & - D_e J^2(J+1)^2 - \alpha_e(v + \frac{1}{2}) J(J+1) \quad . \end{aligned}$$

where

$$(1.8) \quad \omega_e = a \sqrt{2D/\mu}$$

$$(1.9) \quad x_e = \omega_e/4D$$

$$(1.10) \quad B_e = (2\mu R_e^2)^{-1}$$

$$(1.11) \quad D_e = 4B_e^3/\omega_e^2$$

$$(1.12) \quad \alpha_e = 6(\sqrt{\gamma x_e B_e^3/\omega_e} - B_e^2/\omega_e) \quad .$$

Equations (1.6) and (1.8) give

$$(1.13) \quad \gamma = \omega_e^2 \mu \quad .$$

In (1.7) the constant term, $-D$, and the ω_e or B_e terms are precisely those which arise in the case of a harmonic oscillator with force constant γ or a rigid rotator with an internuclear separation R_e , respectively.

Energy formulas for experimental energy levels are usually determined by including higher powers of $(v + \frac{1}{2})$ and $J(J+1)$ and, in the notation of the Bohr theory, they appear in the form

$$(1.14) \quad T_{vJ} = -D + G(v) + F_v(J)$$

where

$$(1.15) \quad G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \\ + \omega_e z_e(v + \frac{1}{2})^4 + \dots$$

$$(1.16) \quad F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \dots$$

$$(1.17) \quad B_v = B_e - \alpha_e(v + \frac{1}{2}) + \gamma_e(v + \frac{1}{2})^2 - \delta_e(v + \frac{1}{2})^3 + \dots$$

$$(1.18) \quad D_v = D_e + \beta_e(v + \frac{1}{2}) + \dots$$

In a more compact notation, (1.14) may be written

$$(1.19) \quad T_{vJ} = \sum_{\ell, j=0} Y_{\ell j} (v + \frac{1}{2})^{\ell} J^j (J+1)^j$$

where the identification with the coefficients of (1.15)-(1.18) is obvious.

Dunham has shown [39], in his studies of the finer interactions of vibrational and rotational motions, that if the radial internuclear potential (1.2) is of the form

$$\begin{aligned}
 U_D(R) = & -D + a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + \dots) \\
 (1.20) \quad & + B_e J(J+1) (1 - 2\xi + 3\xi^2 - \dots),
 \end{aligned}$$

where $\xi = (R - R_e)/R_e$, the energy levels will satisfy an equation of the form (1.19) with $Y_{\ell j}$'s which he gives in terms of μ and the coefficients of (1.20). For B_e/ω_e small, the band spectrum constants resulting from Dunham's procedure are approximately equal to the ones appearing in the Morse solution (1.7).

Thus, by introducing the effects of the anharmonicity of $U(R)$, the energy levels and band spectrum constants are seen to deviate from those given by the ideal relations

$$\begin{aligned}
 D^* &= -V(R_e) \\
 (1.21) \quad \omega_e^* &= (\gamma/\mu)^{1/2} \\
 B_e^* &= (2\mu R_e^2)^{-1}
 \end{aligned}$$

satisfied by the Morse solution.

In Van Vleck's analysis [40] of the dependence of molecular constants upon μ in the various isotopic species of a diatomic molecule, estimates were obtained of certain corrections which cause the μ -dependence of

experimentally-determined values of D , ω_e , and B_e to deviate from that given by (1.21). The corrections considered by Van Vleck are due to (a) the effect of anharmonicity, (b) the coupling between vibrational and electronic motion and the fact that the center of mass of the nuclei is not the same as the center of mass of the molecule, and (c) and (d), the error introduced by the separation of nuclear coordinates in the wave function of the molecule. He derived expressions for the (b), (c) and (d) corrections to ω_e and B_e and estimated them for the case of H_2 , HD , and D_2 by using the Wang wave function. He derived a theoretical estimate of the error resulting from the assumption of infinite nuclear masses which, with known corrections for the separated atoms, can be used to correct D . He expressed the corrections to the "ideal" quantities (1.21) in the form

$$\begin{aligned}
 D &= D^* + \Delta_a + \Delta_s \\
 (1.22) \quad \omega_e &= \omega_e^* (1 + \delta_a + \delta_s) \\
 B_e &= B_e^* (1 + \gamma_a + \gamma_s) .
 \end{aligned}$$

The subscript "a" refers to the anharmonicity correction and the subscript "s" refers to the sum of the (b)-(d) corrections. In the present work, the term values are found by solving (1.1) by the numerical method of Chapter IV. Consequently, the molecular constants derived

from them, which will be distinguished by the superscript "***", need only be corrected for the (b)-(d) effects. In Van Vleck's treatment, the correction formulas may be written

$$\begin{aligned}
 D &= D^{**} + \Delta_s \\
 (1.23) \quad \omega_e &= \omega_e^{***} (1 + \delta_s) \\
 B_e &= B_e^{***} (1 + \gamma_s) .
 \end{aligned}$$

For the purpose of comparing the various corrections to the ideal quantities (1.21), an estimate of the anharmonicity correction may be derived from the relations

$$\begin{aligned}
 D^{**} &= D^* + \Delta_a \\
 (1.24) \quad \omega_e^{**} &= \omega_e^* (1 + \delta_a) \\
 B_e^{**} &= B_e^* (1 + \gamma_a) .
 \end{aligned}$$

Before forming quantitative relations between experimental data and an internuclear potential, some considerations of the magnitude of the uncertainty of each quantity involved must be made. These are:

(1) Van Vleck's corrections (b), (c), and (d), are based on estimates of their effects on the harmonic oscillator and rigid rotator and, consequently, cannot be applied to quantities resulting from motions departing too greatly from these

idealized situations.

(2) The values of D_e^* , B_e^* , and particularly ω_e^* are quite sensitive to both random and systematic errors in $V(R)$.

(3) Calculated term values T_{vJ}^{**} are affected by the systematic errors in $V(R)$ which result from the fact that the accuracy of trial electronic wave functions may vary over the range of R . Furthermore, with a fixed number of values of $V(R)$, the numerical accuracy of T_{vJ}^{**} decreases with increasing v .

(4) There is a certain amount of ambiguity in the definition of the band spectrum constants. In practice one finds that the polynomials in $v + \frac{1}{2}$ and $J(J+1)$ which one tries to fit to the vibrational and rotational levels alternate in sign and, consequently, their coefficients depend, quite critically, upon the number of term values T_{vJ} used, the type of fitting (i.e., exact, least squares, etc.), and the accuracy of the term values. An even more basic difficulty is that low order polynomials in $v + \frac{1}{2}$ and $J(J+1)$ having coefficients ω_e and B_e which can be used to determine γ and R_e simply fail to represent the totality of term values.

A brief perusal of the derivation of band spectrum constants from experimental and theoretical data tends to indicate that in the calculation of the coefficients of

$F_v(J)$, (1.16), most of the indeterminacy is caused by the rapid loss of significant digits in the successive coefficients rather than a failure of the energy formula (1.16). Results also indicate that the effect of the ambiguity in B_v is small relative to both the Van Vleck correction to B_e and the numerical and experimental errors. The difficulties arise when one tries to fit polynomials in $v + \frac{1}{2}$ to the values of $G(v)$, B_v , D_v , ... or their differences. An unambiguous comparison with experiment can be made, however, by considering the vibrational quanta

$$(1.25) \quad \nabla G(v) = G(v) - G(v-1) = \omega_e - 2\omega_e x_e v + \dots$$

For the lowest vibrational states, ω_e is much larger than the sum of all other terms in (1.25) so that one can, within the framework of Van Vleck's assumptions, apply his correction to the vibrational quanta $\nabla G(v)$ instead of ω_e and obtain a more direct comparison with observed spectra. Furthermore, since the correction is in the form of a multiplicative factor, a properly corrected ω_e will result no matter what type of curve-fitting is used to determine the coefficients of (1.25) from the corrected vibrational quanta. By the same argument, one may also apply Van Vleck's B_e correction factor to the rotational term values $F_v(J)$ and to the

rotational constants B_v . These considerations form the basis for the procedure used in Chapter VII for comparing the calculated and experimental spectral data for H_2 , HD, and D_2 .

2. Averaging over R.

After having obtained numerical solutions $S(R)$, $T(R)$, ... of the radial Schroedinger equation, one may proceed to calculate expectation values and transition matrix elements

$$(2.1) \quad \bar{Q} = \int_0^{\infty} S(R) Q(R) T(R) dR$$

corresponding to an operator $Q(R)$. Denoting the integrand by $f(R)$ and assuming that R_{n+1} is so large that $f(R)$ and all of its derivatives are negligible at $R = R_{n+1}$, the Eulerian sum formula* gives

$$(2.2) \quad \bar{Q} \approx \int_0^{R_n} f(R) dR = h \sum_{i=1}^n f_i + \frac{h}{2} f_0 - \frac{h^2}{24} f'_0 + \frac{7h^4}{5760} f'''_0 - \dots$$

where

$$f_i = f(R_i) .$$

In most cases the solutions $S(R)$, $T(R)$, ... and the operator $Q(R)$ are such that $f(R)$ and its derivatives to high order are zero at $R = 0$. Therefore, the trapezoidal rule, which results from neglecting derivatives in (2.2), is an integration formula of quite high order accuracy in h .

* Equation (5.8.20), Page 154, Ref. [41].

VI AN LCAO CALCULATION FOR H_2^+

1. Introduction.

It is immediately obvious, in a calculation of this type, that it would be desirable to vary as many wave function parameters as possible to minimize the electronic energy. However, for many-electron molecules, the computing effort involved in obtaining all the integrals required in a full variation of the orbital exponents of the AO's would make the cost of such computations prohibitive. On the other hand, as one can see from the form of the STO's (II 4.1), applying a scale factor η to all orbital exponents is equivalent to applying the scale factor to all electronic distances in the molecule. The special role of the parameter η and methods for optimizing it have been discussed by Löwdin [42]. Such methods are particularly convenient since expectation values of the potential and kinetic energies of the electrons and the integrals used to compute them satisfy

$$(1.1) \quad V(R, \eta) = \eta V(R \eta, 1)$$

and

$$(1.2) \quad T(R, \eta) = \eta^2 T(R \eta, 1) ,$$

respectively. This means, in effect, that a table giving the integrals as functions of R , with $\eta = 1$, can be

used to obtain the integrals for arbitrary R and η . Furthermore, the same tabular values used to interpolate the integrals can also be used to evaluate the R -derivatives of V and T in Löwdin's formula for $\partial E / \partial \eta$.

The H_2^+ molecule, which does not require the complicated two-electron integrals, is an excellent test case for studying the role of the orbital exponents and for comparing the results of varying a scale factor with the results of varying the orbital exponents independently.

In addition to the above reasons for carrying out a calculation of approximate solutions where exact analytic solutions have already been obtained [43], there is some interest in having theoretical values for certain quantities which can be calculated with these approximate solutions and the machine programs written during the course of this work.

2. Solution of the Electronic Wave Equation.

In the present calculations, the electronic ground state $2\sum_g^+$ was considered and the $1s$, $2s$, and $2p\sigma$ AO's on the two centers were used. Due to the symmetry of the molecule, the respective orbital exponents μ_{1s} , μ_{2s} , and $\mu_{2p\sigma}$ were the same on each center and there were only three g -type MO's to consider. The MO's were calculated by the method described in Section II.4

and the 3×3 matrix \underline{H} of the Hamiltonian

$$(2.1) \quad \mathcal{H} = -\frac{1}{2}\Delta - r_a^{-1} - r_b^{-1}$$

with respect to the g-type MO's was diagonalized.

The calculation was programmed as a subroutine which, for a given internuclear distance R and a given set of three orbital exponents, μ_{1s} , μ_{2s} , and $\mu_{2p\sigma}$, yielded three \sum_g^+ wave functions and energies. For the rest of the discussion, the lowest of these energies, which is an approximation to the electronic ground state of H_2^+ , will be referred to as a function $E(R, \mu_{1s}, \mu_{2s}, \mu_{2p\sigma})$ of the four parameters given to the subroutine.

3. Internuclear Force Curve.

For an exact solution of the electronic wave equation, the internuclear force due to the electrons in a molecule is given by the Virial Theorem (VT)

$$(3.1) \quad dE/dR = -(2T + V)/R$$

where T , V , and E are the kinetic, potential, and total energies, respectively, of the electrons. Under the same conditions, the internuclear force is also given by the Hellman-Feynman Theorem (HFT),

$$(3.2) \quad dE/dR = \left\langle \sum_{i=1}^N r_{ai}^{-2} \cos \theta_{ai} \right\rangle_{av.el.}$$

The right side of (3.2) represents the average value, over electronic coordinates, of the electric field at nucleus A due to the electronic charge cloud. It can easily be shown* that the VT will be satisfied by a wave function for which a scale factor, applied to electronic coordinates, minimizes E at each R . Here, and in what follows, "minimize E " will imply that, at the value of the parameter in question, E is a continuous differentiable function of the parameter and has a relative, but not necessarily an absolute, minimum. Hurley [44] has discussed the conditions under which approximate wave functions satisfy both the VT and the HFT. Hurley's results, in the present application, show that the HFT will be satisfied if all parameters in the electronic wave function which are allowed to vary with R minimize E at each R . The linear coefficients of the MO's and optimized orbital exponents satisfy these requirements. The one remaining R -dependent parameter in the present wave function gives the locations of the centers of the AO's. Hurley's results imply that the HFT would have been satisfied if the calculation had been performed with floating orbitals, i.e., orbitals having centers, not at the nuclei, but at symmetric points on the nuclear axis determined by minimizing E with respect to the distance between them. (Use of

* See Löwdin, Ref. [42].

floating orbitals would necessitate the use of some three-center nuclear attraction integrals and would have introduced one more nonlinear parameter in the variation process.)

The variation of orbital exponents was performed in two ways. In the first, which will be called Case A, all the orbital exponents were set equal to η . At each of the internuclear distances $R = .125(.125)10$ one or two values of η which minimize $E(R, \eta, \eta, \eta)$ were found. Letting $\eta(R)$ denote the value of η which gives the lower minimum of E , $\eta(R)$ was found to jump from one continuous curve to another between $R = 4.250$ and $R = 4.375$. The $\eta(R)$ curve is plotted in Figure 5 with nonconnected points indicating values of η where the higher minima were found.

The results of the calculations indicate that if one optimizes η at a relatively few points and interpolates to get values of $\eta(R)$ at other points, one must optimize η at enough values of R to establish that the points used in each application of the interpolation formula lie on the same continuous curve. One further consequence of the discontinuous $\eta(R)$ curve is that the VT and HFT will not hold at points of discontinuity in $\eta(R)$ or at points obtained by interpolating across such discontinuities.

In the second calculation, which will be called Case B, the three orbital exponents μ_{1s} , μ_{2s} , and $\mu_{2p\sigma}$ were

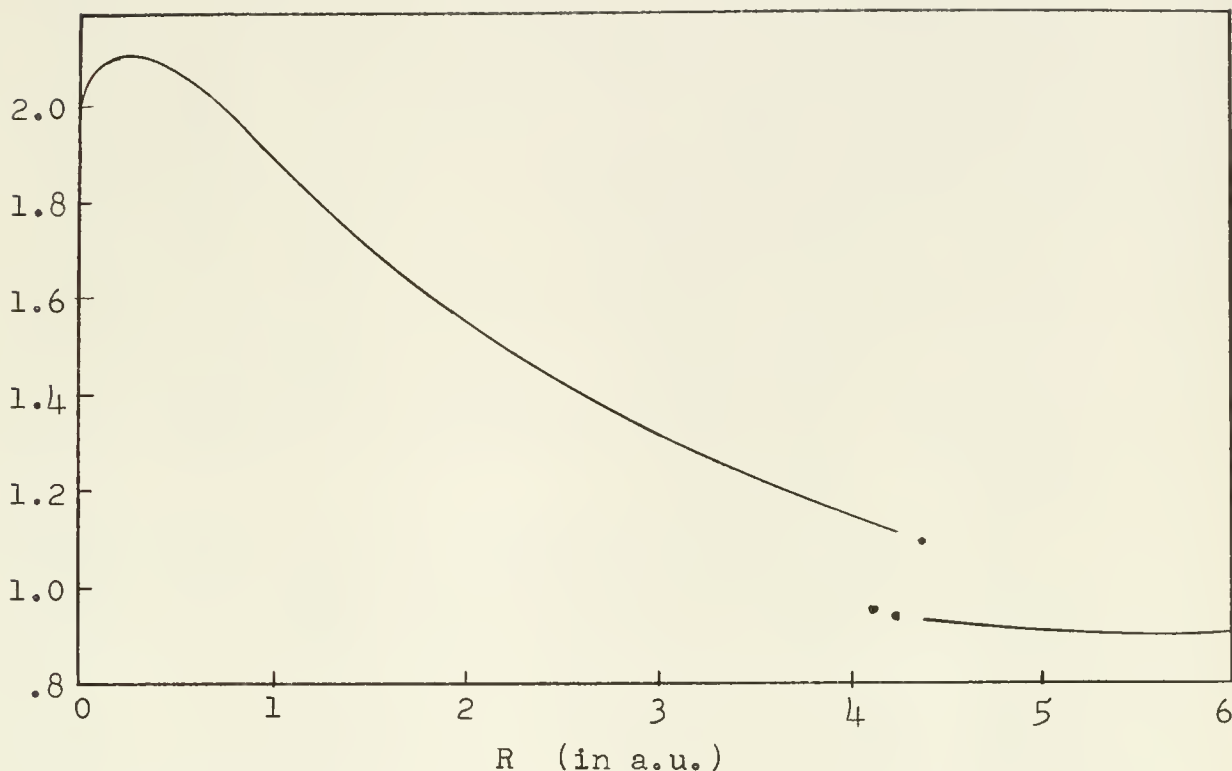


Fig. 5. Graph of Optimal Scale Factor $\eta(R)$

varied independently by the procedure described in Section II 10. This added the following complications to the problem:

1. There were more minima at each R . For example, six minima were found at $R = 2.0$.

2. More points were found where the best minimum changed from one continuous curve in the $(R, \mu_{1s}, \mu_{2s}, \mu_{2po})$ -space to another.

3. The energy surface defining E as a function of the μ 's for fixed R was often quite flat in a diagonal direction in the $\mu_{1s}-\mu_{2s}$ plane. For this reason, fewer significant digits could be calculated for μ_{1s} and μ_{2s} .

The implication of these results is that so little significance can be attached to interpolated values of optimal μ 's that it is of dubious value to spend much computing effort on optimizing the μ 's at a few points and then interpolating to obtain the rest. Instead, it would probably be better to optimize the μ 's independently at one point near R_e , the equilibrium value of R , and optimize only a scale factor on the resulting μ 's at all other values of R .

In order to check the numerical results and to make one further point, the numerical derivative,

$$E'_N = (E(R + .05) - E(R - .05)) / .1 ,$$

of the $E(R)$ of Case B was calculated and compared with the values given by formulas (3.1) and (3.2). The latter will be denoted by E'_{VT} and E'_{HFT} , respectively. Some of the results are given in Table 5. It was found that the discrepancy between E'_N and E'_{VT} was less than the error of the numerical differentiation formula. The numerical results obtained here also provided some interesting information about the validity of the assumption, made by some workers, that the force constant can be evaluated by supposing that the electronic charge cloud is approximately stationary for R near the equilibrium distance R_e . Under this assumption, one can differentiate the expectation

TABLE 5. ELECTRONIC ENERGY OF H_2^+ AND ITS DERIVATIVES

R	$E_{\text{el}}(R)$	E'_N	E'_{VT}	E'_{HFT}	$\partial^2 E / \partial R^2$	$Q_{\text{zz}}(R)$
.25	-1.398 485	.619 602	.622 391	.621 515	.751 64	.881 412
.50	-1.234 853	.648 126	.648 659	.647 820	-.239 23	.754 080
.75	-1.002 259	.566 998	.567 150	.567 322	-.371 39	.571 244
1.00	-.951 662	.479 176	.479 169	.479 945	-.333 75	.428 079
1.25	-.841 639	.403 405	.403 215	.405 624	-.276 02	.325 528
1.50	-.748 765	.341 830	.341 777	.343 183	-.220 01	.248 946
1.75	-.669 813	.291 661	.291 588	.293 210	-.180 40	.193 306
2.00	-.602 199	.250 704	.250 759	.252 522	-.147 58	.152 152
2.25	-.543 871	.217 068	.217 026	.219 044	-.121 64	.121 284
2.50	-.493 223	.189 767	.189 042	.191 191	-.102 39	.097 586
2.75	-.448 903	.165 555	.165 583	.167 662	-.086 70	.078 820
3.00	-.410 072	.145 871	.145 559	.147 622	-.074 93	.064 232
3.25	-.375 883	.128 364	.128 349	.130 737	-.064 74	.052 754
3.50	-.345 685	.113 547	.113 529	.116 029	-.055 06	.043 494
4.00	-.295 236	.089 337	.089 364	.091 871	-.042 34	.029 914
5.00	-.223 829	.056 340	.056 355	.058 722	-.025 33	.014 762

value of the electronic energy twice, with nucleus B

held fixed, to get

$$\begin{aligned} \partial^2 E / \partial R^2 &\approx \langle \partial^2 \mathcal{H} / \partial R^2 \rangle_{\text{av.el.}} = - \left\langle \sum_{i=1}^N (3 \cos^2 \theta_{ai} - 1) r_{ai}^{-3} \right\rangle_{\text{av.el.}} \\ (3.3) \quad &= - Q_{zz}(R) . \end{aligned}$$

Values of $\partial^2 E / \partial R^2$, obtained from central differences of E'_{VT} , and $Q_{zz}(R)$, the electric field gradient along the molecular axis at nucleus A, are listed in Table 5 where it may be observed that $\partial^2 E / \partial R^2$ and $-Q_{zz}(R)$, although quite different for most values of R , differ by only 3% at $R = R_e = 2.00$. It has been shown by W. Clinton [45] that the assumption of a static charge cloud, taken with the VT and HFT, leads to contradictions and, is therefore invalid. He also points out that deceptively good agreement, based on this false assumption, does seem to occur with the use of LCAO wave functions. This observation is supported by the present calculation where there is a discrepancy of only 3% between $-\partial^2 E / \partial R^2$ and $Q_{zz}(R)$ at $R = 2.00$ while, in the more accurate non-LCAO calculation of Auffray and Cooley [46] $Q_{zz}(2)$ is 18% greater than $-\partial^2 E / \partial R^2|_{R=2}$.

The dissociation energy in Case A was .102 185 a.u., for Case B it was .102 199 a.u., and in the accurate calculation of Auffray and Cooley, it was .102 634 a.u. For other values of R , the difference between Case A and Case B was slightly greater but hardly enough to warrant the amount of calculation involved in varying three nonlinear parameters instead of one.

VII CALCULATIONS FOR H_2 , HD, AND D_2

1. The Electronic Wave Functions and Internuclear Potentials.

The results reported in this chapter were calculated with two different electronic wave functions for the $1\Sigma_g^+$ state. The first of these was calculated by McLean, Weiss, and Yoshimine [47] (hereafter referred to as MWY) and was of the form

$$(1.1) \quad \Psi = \sum_{k=1}^5 c_k \Psi_k$$

where

$$(1.2) \quad \begin{aligned} \Psi_1 &= (1s_g, 1s_g), \quad \Psi_2 = (2s_g, 2p\sigma_g), \\ \Psi_3 &= (1s_u, 1s'_u), \quad \Psi_4 = (2p\pi_u, 2p\pi_u), \\ \Psi_5 &= (2p\pi_g, 2p\pi_g). \end{aligned}$$

Since an antisymmetric spin function can conveniently be factored out, Ψ is constructed as a symmetric function of space coordinates. The notation in (1.2) denotes the symmetrized products

$$(1.3) \quad (\chi, \chi') = \chi(1) \chi'(2) + \chi(2) \chi'(1)$$

where the one-electron space functions are nonorthonormalized primitive symmetry orbitals,

$$(1.4) \quad \chi_{g \text{ or } u} = 2^{-\frac{1}{2}} (\chi_a \pm \chi_b),$$

constructed of the AO's in (II 4.1). The STO's $1s$ and $1s'$ in Ψ_3 differ only in the orbital exponent. The five orbital exponents μ_{1s} , $\mu_{1s'}$, μ_{2s} , $\mu_{2p\sigma}$, and $\mu_{2p\pi}$ were optimized at five internuclear distances and their values at the remaining points were obtained by interpolation. MWY state that a minimum was assumed to have been found when three significant figures agreed in the binding energy on successive iterations. However, in the minimizing for H_2^+ described in the previous chapter, where seven significant figures was the criterion, there were six minima, at $R = R_e$, all agreeing in the first three digits but having quite different orbital exponents. Therefore, MWY's orbital exponents are possibly not the ones for the absolute minima. This, and the possibility of a discontinuous optimal orbital exponent curve lead one to doubt the accuracy of the interpolated orbital exponents. The present author would suggest the possibility that a more thorough calculation of optimal orbital exponents near the equilibrium distance, followed by a variation of a scale factor for other values of R would have given a better internuclear potential curve with about the same amount of effort.

With the orbital exponents so determined, MWY calculated the coefficients C_k of (1.1) at 45 non-uniformly spaced points in the range $.8 \leq R \leq 6.0$.

In the present calculation, the values of

$$(1.5) \quad W^{(n)}(R) = \int \Psi^* \sum_{i=1}^2 r_{ai}^{-n-1} n! P_n(\cos \theta_{ai}) \Psi dV,$$

where P_n is the n -th Legendre polynomial, were obtained for $n = 0, 1$ and 2 at each value of R for which MWY gave the wave function parameters. The program which calculated these average values was used to calculate the normalization factor as a check. Then, the values of (1.5) and the electronic energy $E_{e1}(R)$ were obtained at the equally-spaced points $R = 0(.02)6$ by quadratic interpolation. This permitted the use of the program described in Chapter IV to calculate the nuclear wave functions. The spacing $h = .02$ is that given by MWY around the equilibrium value of R . The maximum R given by MWY was found, by numerical trials, to be high enough to solve the radial Schroedinger equation. For the low range of R , the two lowest calculated points, $R = .8$ and $R = .9$, and values at $R = 0$ appropriate to the united atom, H_e , were used by the interpolation procedure. Errors introduced in the internuclear potential for low R were relatively small due to the large Coulomb repulsion term $1/R$ and would be of importance only if one were to try to go to higher vibrational levels.

The second electronic wave function was calculated by Kolos and Roothaan [48] (hereafter referred to as KR) and

was of the form

$$(1.6) \quad \Phi = \sum_i c_i \Phi_i$$

where

$$\Phi_i = \Psi(p_i, q_i, r_i, s_i, \mu_i) + \Psi(r_i, s_i, p_i, q_i, \mu_i)$$

$$\Psi(p, q, r, s, \mu) = e^{-a(\xi_1 + \xi_2)} \xi_1^p \eta_1^q \xi_2^r \eta_2^s r_{12}^\mu$$

Here, ξ and η are the elliptic coordinates and a is a scale factor which was optimized at each of the internuclear distances at which the calculation was performed. Except for large R , the KR electronic energies are lower than those obtained with the MWY wave function. The internuclear potential for the full range of R , at intervals of .05 a.u., was obtained by using MWY's values for high R and by interpolating as described above. The equilibrium energies for the MWY and KR potentials were $36\,644.09 \text{ cm.}^{-1}$ and $38\,285.60 \text{ cm.}^{-1}$, respectively.

2. Vibrational-Rotational Spectrum.

A large number of vibrational-rotational wave functions and term values for H_2 , HD, and D_2 were calculated with both the MWY and the KR internuclear potentials using the reduced masses

$$\mu = 918.06 \quad \mu' = 1223.77 \quad \mu'' = 1834.7094$$

for H_2 , HD, and D_2 , respectively. Some of the term values obtained with the more accurate KR potential are listed in Table 6 with the zero-point taken as the energy (-1 a.u.) of the dissociated atoms, $H(1s) + H(1s)$.

The corrections estimated by Van Vleck for H_2 , HD, and D_2 , which will be used here, are, in the notation of (V 1.23),

$$\begin{aligned}
 \Delta_s &= 5.5 \text{ cm}^{-1} & \Delta'_s &= 4.6 \text{ cm}^{-1} & \Delta''_s &= 2.8 \text{ cm}^{-1} \\
 (2.1) \quad \delta_s &= -.00071 & \delta'_s &= -.00052 & \delta''_s &= -.00035 \\
 \gamma_s &= -.00089 & \gamma'_s &= -.00068 & \gamma''_s &= -.00044
 \end{aligned}$$

where the unprimed, primed, and double-primed quantities are for H_2 , HD, and D_2 , respectively.

The vibrational quanta (1.25) obtained by using the MWY and KR potentials are listed in Table 7. The result of applying the Van Vleck corrections to the vibrational quanta obtained with the KR potential are given in column four for comparison with the experimental values in column five. It may be observed that the MWY vibrational quanta are too small by an amount which increases almost linearly in magnitude from 12 cm^{-1} at $v = 1$ to 53 cm^{-1} at $v = 6$ while the KR results are too large by an amount which increases only slightly from 8 cm^{-1} at $v = 1$. For $v > 6$, the discrepancy in both cases is in the same

TABLE 6. CALCULATED^a TERM VALUES ($-T_{vJ}$), BELOW DISSOCIATION LIMIT, FOR H_2 , HD, and D_2 (IN CM^{-1}).

	$v \backslash J$	0	1	2	3
H_2	0	36 103.50	35 984.89	35 748.74	35 397.21
	1	31 934.21	31 821.49	31 597.10	31 263.11
	2	28 001.14	27 894.18	27 681.26	27 364.40
	3	24 296.84	24 195.55	23 993.93	23 693.93
	4	20 816.97	20 721.21	20 530.64	20 247.16
	5	17 561.38	17 471.18	17 291.69	17 024.73
	6	14 527.22	14 442.64	14 274.39	14 024.22
HD	0	36 393.15	36 303.83	36 125.80	35 860.28
	1	32 754.17	32 668.69	32 498.33	32 244.27
	2	29 293.92	29 212.20	29 049.35	28 806.51
	3	26 006.28	25 928.29	25 772.85	25 541.10
	4	22 889.35	22 814.95	22 666.68	22 445.64
	5	19 941.07	19 870.32	19 729.34	19 519.19
	6	17 158.11	17 090.95	16 957.18	16 757.82
D_2	0	36 737.72	36 677.87	36 558.47	36 380.04
	1	33 738.70	33 680.95	33 565.74	33 393.58
	2	30 860.53	30 804.86	30 693.78	30 527.82
	3	28 097.83	28 044.20	27 937.19	27 777.31
	4	25 453.09	25 401.43	25 298.38	25 144.41
	5	22 918.88	22 869.25	22 770.22	22 622.29
	6	20 499.70	20 451.95	20 356.68	20 214.38

*Calculated with Kolos and Roothaan's internuclear potential [48].

TABLE 7. CALCULATED AND OBSERVED VIBRATIONAL QUANTA
 $\nabla G(v)$ FOR H_2 , HD, AND D_2 (IN CM^{-1}).

	MWY ^a	KR ^b	KR, Corr.	Exp.
H_2	1 4149.20	4169.29	4166.33	4161.13 ^c
	2 3908.11	3933.07	3930.28	3925.95
	3 3670.38	3704.30	3701.67	3695.24
	4 3434.24	3479.87	3477.40	3468.01
	5 3198.55	3255.59	3253.28	3241.56
	6 2959.64	3034.16	3032.01	3013.73
HD	1 3622.14	3638.98	3637.09	3632.14 ^d
	2 3440.77	3460.25	3458.45	3454.73
	3 3261.20	3287.64	3285.93	3280.68
	4 3084.46	3116.93	3115.31	3109.31
	5 2906.80	2948.28	2946.75	
	6 2730.17	2782.96	2781.51	
D_2	1 2985.74	2999.02	2997.97	2993.548 ^e
	2 2864.53	2878.17	2877.16	
	3 2743.36	2762.70	2761.73	
	4 2625.57	2644.74	2643.81	
	5 2506.48	2534.21	2533.32	
	6	2419.18	2418.33	

^aCalculated with McLean, Weiss, and Yoshimine's internuclear potential [47].

^bCalculated with Kolos and Roothaan's internuclear potential [48].

^cHerzberg and Howe [51].

^dDurie and Herzberg [50].

^eStoicheff [49].

direction and increases in magnitude with v . This can partly be attributed to the nature of the electronic wave functions used by MWY and KR. The LCAO wave functions of MWY, for obvious reasons, give better electronic energies at the extreme values of R but yield an internuclear potential which is too shallow in the intermediate range. On the other hand, the KR electronic wave function is better for the intermediate range of R and, consequently, curves upward too much for R very different from R_e . The effect is as one may expect: the low curvature of the MWY potential causes the vibrational levels to lie too close together and the high curvature of the KR potential causes them to lie too far apart. However, one would not expect the error in curvature of the KR potential to be significant for the lowest vibrational states.

An unambiguous test of the theoretically-calculated rotational effects and of the value of R_e given by the KR potential can be made by a comparison with the pure rotation Raman S-lines measured by Stoicheff [49]. These are given by the differences

$$(2.1) \quad S_v(J) = F_v(J+2) - F_v(J)$$

In Table 8, Stoicheff's values, which are reportedly accurate to $\pm .02 \text{ cm.}^{-1}$, are listed with the results of applying the Van Vleck correction to the differences (2.1)

obtained from the KR potential.

TABLE 8. CALCULATED^a AND OBSERVED^b RAMAN $S_0(J)$ LINES
OF H_2 , HD, AND D_2 .

	H_2			HD			D_2		
	Calc.	Exp.	% Dif	Calc.	Exp.	% Dif	Calc.	Exp.	% Dif
$S_0(0)$	354.44	354.38	.02	267.17	267.09	.03	179.17	179.06	.06
$S_0(1)$	587.16	587.06	.02	443.25	443.08	.04	297.70	297.52	.06
$S_0(2)$	814.59	814.41	.02	616.33	616.09	.04	414.89	414.66	.06
$S_0(3)$	1034.91	1034.65	.03	785.32	784.99	.04	530.21	529.91	.06
$S_0(4)$	1246.42			949.19	948.82	.04	643.20	642.81	.06
$S_0(5)$	1447.69			1107.06			753.39		

^aCalculated with KR potential. The Van Vleck correction has been applied.

^bStoicheff [49].

The rotational constants B_v , D_v , and H_v , given in Tables 9 and 10, were calculated by an exact fit of the rotational energy formula (V 1.16) to the $J = 0, 1, 2$, and 3 rotational levels. It was found that using one or more or less J -levels affected B_v only in the last figure given. This and the fact that the percentage deviations from experiment in the Raman S-lines of Table 8 are quite close to those for the B_v values of Table 9 indicate that the uncertainty due to the procedures for obtaining the B_v 's is negligibly small.

TABLE 9. CALCULATED AND OBSERVED ROTATIONAL CONSTANTS

 B_v FOR H_2 , HD, AND D_2 (IN CM^{-1}).

	v	MWY ^a	KR ^b	KR, Corr.	Exp.
H_2	0	59.283	59.398	59.345	59.339 ^c
	1	56.271	56.449	56.399	56.369
	2	53.310	53.567	53.519	53.475
	3	50.390	50.732	50.687	50.626
	4	47.448	47.961	47.918	47.801
	5	44.505	45.181	45.141	44.958
	6	41.489	42.365	42.327	42.096
HD	0	44.629	44.712	44.682	44.668 ^d
	1	42.665	42.790	42.761	42.742
	2	40.734	40.905	40.877	40.838
	3	38.833	39.047	39.020	38.998
	4	36.923	37.251	37.226	37.140
	5	35.026	35.421	35.397	
	6	33.087	33.620	33.597	
D_2	0	29.890	29.943	29.930	29.910 ^e
	1	28.816	28.894	28.881	28.848
	2	27.759	27.857	27.845	
	3	26.716	26.838	26.826	
	4	25.681	25.847	25.836	
	5	24.627	24.840	24.829	
	6		23.896	23.885	

^aCalculated with McLean, Weiss, and Yoshimine's inter-nuclear potential [47].^bCalculated with Kolos and Roothaan's internuclear potential [48].^cHerzberg and Howe [51].^dDurie and Herzberg [50].^eStoicheff [49].

TABLE 10. CALCULATED AND OBSERVED ROTATIONAL CONSTANTS

 D_v AND H_v FOR H_2 , HD, AND D_2 (IN CM^{-1}).

	MWY ^a		KR ^b		Exp.			
v	D _v	H _v x 10 ⁵	D _v	H _v x 10 ⁵	D _v		H _v x 10 ⁵	
H ₂	0	.0456	2.4	.0456	3.6	.0459 ^c	.0459 ^d	5.2 ^c
	1	.0444	5.2	.0443	5.4	.0432	.0437	
	2	.0430	3.0	.0427	4.8	.0427	.0427	
	3	.0416	4.0	.0414	5.7	.0412	.0409	3.75 ^d
	4	.0406		.0404			.0397	3.50
	5	.0399		.0389			.0385	3.4
	6			.0385			.0377	3.3
HD	0	.0259	3.5	.0257	1.9	.0259 ^c	.0263 ^d	2.2 ^c
	1	.0250	1.1	.0251	2.6	.0255	.0254	
	2	.0244	1.4	.0243	2.7		.0241	
	3	.0237	2.0	.0237	2.3		.0244	
	4	.0232		.0242			.0231	
	5	.0227		.0224				
	6			.0242				
D ₂	0	.0114		.0114	-.1	.0113 ^c		.36 ^c
	1	.0112		.0113	.9	.0107		
	2	.0110		.0110	1.6			
	3	.0107		.0108	1.2			
	4	.0105		.0106				
	5	.0102		.0110				
	6			.0109				

^aCalculated with McLean, Weiss, and Yoshimine's inter-nuclear potential [47].^bCalculated with Kolos and Roothaan's internuclear potential [48].^cStoicheff [49].^dHerzberg and Howe [51].

The discrepancy of $-.012\%$ in the equilibrium values, $R_e = 1.40100$ and $R_e = 1.40083$, of the MWY and KR potentials, respectively, would correspond to a discrepancy of $.006\%$ in B_v for the rigid rotator. Consequently, the difference of approximately $.2\%$ in the calculated B_v values must be due to the poorer anharmonicity of the MWY potential.

The experimental and calculated data for the $v = 0$ vibrational level of the heaviest isotope, D_2 , should provide the best comparison of the theoretical and experimental R_e since this is the case where R is nearest to R_e during the vibrational motion and where Van Vleck's corrections are smallest and most accurate. In Tables 8 and 9 it is seen that the calculated $S_0(J)$ and B_v values are approximately $.06\%$ higher than the experimental ones. This implies that, if one accepts the Van Vleck correction, the calculated R_e of the KR potential is $.03\%$ lower than the experimental evidence indicates it should be. However, the figure of $.06\%$ is so close to the Van Vleck correction of $.044\%$ to B_e and to the numerical and experimental errors that this can only be accepted as an order of magnitude estimate.

The calculation of the anharmonicity corrections defined in (V 1.24) is described in Table 11. The value of γ , which is used to calculate ω_e^* , was obtained by

TABLE 11. CALCULATION OF ANHARMONICITY CORRECTION^a

	H ₂	HD	D ₂
D [*]	38 285.59	38 285.59	38 285.59
D ^{**}	38 279.06	38 281.56	38 284.23
Δ_a	6.53	4.03	1.36
B _e [*]	60.913	45.699	30.480
B _e ^{**}	60.905	45.690	30.470
γ_a	-.00013	-.00020	-.00033
ω_e^*	4410.99	3820.51	3120.24
ω_e^{**}	4412.67	3823.54	3125.04
δ_a	-.00038	-.00079	-.00154

^aThe "*" denotes quantities derived from the equilibrium constants $D = .174\ 442$ a.u., $R_e = 1.40083$ a.u., and $\gamma = .37083$ a.u. obtained from the Kolos and Roothaan potential [48]. The "**" denotes quantities obtained by an exact fit of the energy formula to the calculated $v = 0, 1, 2, 3$, $J = 0, 1, \dots, 4$ term values.

numerical differentiation of the slope of the internuclear potential as given by the Virial Theorem.

The calculated molecular constants obtained with the KR potential are summarized in Table 12. The calculated quantities in parentheses were obtained by applying the Van Vleck corrections (2.1). The experimental quantities in parentheses are of doubtful accuracy due to a lack of experimental evidence. It must be remembered that all calculated quantities with the subscript "e" are, for the reasons given above, subject to some uncertainty due to

TABLE 12. VIBRATIONAL-ROTATIONAL CONSTANTS OF

 H_2 , HD , AND D_2 (IN cm^{-1}).

	H_2		HD		D_2	
	Calc.	Exp. ^{a,d}	Calc.	Exp. ^{b,d}	Calc.	Exp. ^{c,d}
B_0	59.398 (59.345)	59.339	44.712 (44.682)	44.669	29.943 (29.930)	29.911
B_e	60.905 (60.851)	60.864	45.690 (45.659)	45.663	30.470 (30.457)	(30.442)
α_e	3.037	3.076 4	1.970	2.003	1.054	
γ_e	.04988	.060 1	.026 8	.039 7	.000 6	
δ_e	-.003 5		-.001 8	-.003 4	+.001	
R_e	.741 66Å	.741 58Å	.741 58Å	.741 51Å	.741 57Å	.741 65Å
R_e^*	.741 28Å	.741 16Å	.741 28Å	.741 19Å	.741 28Å	.741 43Å
D_e	.045 92	.046 57	.025 9	.026 7	.011 4	(.011 64)
β_e	-.000 46	-.001 62	-.000 1	-.000 7	.000 05	
H_e	45×10^{-5}		1.5×10^{-5}	2.2×10^{-5}	$-.5 \times 10^{-5}$	
$-T_{00}$	36 103.5 (36 109.0)	36 113.0 \pm .3	36 393.2 (36 397.8)	36 399.9 \pm 1.	36 737.7 (36 740.5)	36 743.6 \pm .5
D^e	38 279.1 (38 284.6)	38 292.3 \pm .5	38 281.6 (38 286.2)	38 290.3 \pm 1.	38 284.2 (38 287.0)	38 290.8 \pm .7
$\nabla G(1)$	4169.29 (4166.33)	4161.14	3638.98 (3637.09)	3632.15	2999.02 (2997.97)	
ω_e	4412.67 (4409.54)	4400.39	3823.54 (3821.55)	3812.29	3125.04 (3123.95)	
$\omega_e x_e$	123.71	120.82	93.935	90.908	64.468	
$\omega_e y_e$	1.243	.724	1.017	.504	.898	

^aHerzberg and Howe [51], with the exception of $-T_{00}$ and D .^bDurie and Herzberg [50], with the exception of $-T_{00}$, D , and H_e . The latter is given by Stoicheff [49].^cStoicheff [49], with the exception of $-T_{00}$ and D .^dThe experimental $-T_{00}$ and D values are those reported by Herzberg and Monfils [52].^eThe calculated D -values given were obtained by fitting the energy formula to the calculated term values. The value of D from Kolos and Roothaan's potential curve is $D = 38\,285.6\text{ cm}^{-1}$.

the ambiguity in their definitions. In the "Calc." columns, R_e^* was obtained directly from the KR potential and R_e was obtained from the calculated B_e after the Van Vleck correction. The values of R_e and R_e^* in the "Exp." columns are those given by the authors of the experimental data and are to be compared with the calculated R_e and R_e^* .

It may be observed in Table 12 that the corrected theoretical energies $-T_{00}$ of H_2 , HD, and D_2 are 4, 2, and 3 cm^{-1} lower than the corresponding experimental values. However, the potential used here was for the 40-term electronic wave function. A 50-term wave function was also calculated by KR for R near R_e and gave a value of D which was 1.5 cm^{-1} higher. Adding this figure to $-T_{00}$ reduces the discrepancy with experiment almost to numerical and experimental error. As Herzberg and Monfils [52] point out, Fröman's [53] estimates of relativistic effects indicate that one may have to add between 3 and 23 cm^{-1} to these theoretical values while electrodynamic (Lamb shift) corrections would require the subtraction of some small amount.

These results indicate that, in addition to giving an accurate binding energy, the KR potential gives a correct prediction of the vibrational-rotational levels and consequently has the correct shape for a wide range

of R-values. This gives one confidence in the accuracy of the nuclear wave functions obtained and used for calculating the expectation values reported in the next section.

3. Expectation Values $\langle R^\ell \rangle_{vJ}$.

The expectation values of powers of internuclear distance were obtained from the solutions of the nuclear wave equation with the KR internuclear potential. The results are given in Tables 13-15 in a.u. It is expected that the use of these results will yield some improvement in the derivation of important physical constants from radiofrequency spectra.

One simple and direct application can be made by referring to Ramsey's [54] measurement of the nuclear spin-spin interaction energy

$$(3.1) \quad d = \frac{4}{5h} \mu_P^2 \langle R^{-3} \rangle_{0,1}$$

of H_2 . Taking, for the proton magnetic moment, $\mu_P = 1.52102 \times 10^{-3}$ Bohr magnetons, Ramsey's experimental findings and the present theoretical results give

$$\langle R^{-3} \rangle_{0,1} = 0.355\ 873 \text{ and } 0.356\ 099 \text{ a.u.}$$

respectively.

TABLE 13. EXPECTATION VALUES $\langle R^\ell \rangle_{vJ}$ for H_2 (IN A.U.)

v	ℓ	J		
		0	1	2
0	-3	.357 756	.356 099	.352 824
	-2	.496 928	.495 404	.492 386
	-1	.700 064	.698 999	.696 882
	1	1.447 989	1.450 165	1.454 505
	2	2.124 832	2.131 178	2.143 864
1	-3	.345 068	.343 419	.340 160
	-2	.472 247	.470 772	.467 851
	-1	.673 263	.672 234	.670 189
	1	1.544 370	1.546 639	1.551 166
	2	2.470 844	2.477 980	2.492 248
2	-3	.331 786	.330 154	.326 932
	-2	.448 140	.446 716	.443 896
	-1	.647 157	.646 163	.644 189
	1	1.644 722	1.647 092	1.651 822
	2	2.852 156	2.860 175	2.876 211
3	-3	.317 837	.316 224	.313 040
	-2	.424 422	.423 043	.420 313
	-1	.621 558	.620 593	.618 679
	1	1.749 848	1.752 343	1.757 321
	2	3.274 379	3.283 436	3.301 546

TABLE 14. EXPECTATION VALUES $\langle R^l \rangle_{vJ}$ FOR HD (IN A.U.)

v	l	J		
		0	1	2
0	-3	.358 558	.357 313	.354 847
	-2	.498 620	.497 474	.495 197
	-1	.701 908	.701 106	.699 511
	1	1.441 594	1.443 222	1.446 472
	2	2.102 454	2.107 177	2.116 620
1	-3	.347 653	.346 413	.343 955
	-2	.477 186	.476 071	.473 857
	-1	.678 618	.677 839	.676 291
	1	1.524 614	1.526 302	1.529 672
	2	2.398 180	2.403 409	2.413 866
2	-3	.336 267	.335 039	.332 605
	-2	.456 168	.455 088	.452 944
	-1	.655 850	.655 097	.653 597
	1	1.610 549	1.612 298	1.615 790
	2	2.719 752	2.725 527	2.737 076
3	-3	.324 350	.323 129	.320 713
	-2	.435 440	.434 387	.432 296
	-1	.633 472	.632 736	.631 273
	1	1.699 952	1.701 782	1.705 434
	2	3.070 828	3.077 253	3.090 099

TABLE 15. EXPECTATION VALUES $\langle R^{\ell} \rangle_{vJ}$ FOR D_2 (IN A.U.).

v	ℓ	J		
		0	1	2
0	-3	.359 506	.358 675	.357 024
	-2	.500 625	.499 858	.498 331
	-1	.704 094	.703 557	.702 487
	1	1.434 048	1.435 131	1.437 294
	2	2.076 185	2.079 306	2.085 546
1	-3	.350 705	.349 875	.348 227
	-2	.483 082	.482 332	.480 838
	-1	.685 010	.684 486	.683 442
	1	1.501 385	1.502 501	1.504 729
	2	2.313 853	2.317 247	2.324 033
2	-3	.341 475	.340 653	.339 021
	-2	.465 737	.465 007	.463 555
	-1	.666 228	.665 719	.664 705
	1	1.570 716	1.571 860	1.574 146
	2	2.568 558	2.572 228	2.579 564
3	-3	.332 006	.331 183	.329 547
	-2	.448 711	.447 991	.446 560
	-1	.647 805	.647 302	.646 302
	1	1.642 079	1.643 273	1.645 657
	2	2.841 480	2.845 507	2.853 560

4. Expectation Values $\left\langle \sum_{i=1}^2 r_{ai}^{-n-1} n! P_n(\cos \theta_{ai}) \right\rangle_{vJ}$.

The expectation values considered here give the average values, over electronic and nuclear coordinates, of the operators

$$(4.1) \quad \sum_{i=1}^2 r_{ai}^{-1}$$

$$(4.2) \quad \sum_{i=1}^2 r_{ai}^{-2} \cos \theta_{ai}$$

$$(4.3) \quad \sum_{i=1}^2 r_{ai}^{-3} (3 \cos^2 \theta_{ai} - 1)$$

where the subscript ai refers to the spherical polar coordinates of electron i referred to nucleus A . The calculated values listed in Table 16 were obtained with the MWY electronic wave function and internuclear potential which, it should be remembered, is less accurate than the KR potential used in the previous sections. Expectation values of (4.1) and (4.3) give the nuclear screening parameter and electric field gradient required in the analysis of radiofrequency spectra. The average, over electronic coordinates, of (4.2) is the electric field at nucleus A which, by the Hellman-Feynman Theorem, is approximately equal to the force on A due to the electrons at the distance R at which (4.2) is calculated. The average of this quantity, over R is then simply an estimate of the expectation value of the electric field at A .

TABLE 16. EXPECTATION VALUES $\left\langle \sum_{i=1}^2 r_{ai}^{-n-1} n! P_n(\cos \theta_{ai}) \right\rangle_{vJ}$
 FOR H_2 , HD , AND D_2 (IN A.U.).

	v	n	J		
			0	1	2
H_2	0	0	1.799 119	1.797 829	1.795 265
		1	.494 280	.493 515	.491 993
		2	.359 572	.358 740	.357 089
	1	0	1.760 313	1.759 086	1.756 649
		1	.469 717	.468 983	.467 523
		2	.338 275	.337 489	.335 928
	2	0	1.722 571	1.721 387	1.719 032
		1	.445 560	.444 844	.443 419
		2	.317 374	.316 626	.315 140
	3	0	1.684 136	1.682 957	1.680 611
		1	.420 307	.419 576	.418 119
		2	.296 563	.295 831	.294 377
HD	0	0	1.801 817	1.800 846	1.798 912
		1	.495 978	.495 402	.494 255
		2	.361 061	.360 434	.359 187
	1	0	1.768 041	1.767 112	1.765 263
		1	.474 633	.474 078	.472 972
		2	.342 563	.341 967	.340 781
	2	0	1.735 229	1.734 337	1.732 560
		1	.453 708	.453 172	.452 104
		2	.324 321	.323 754	.322 625
	3	0	1.702 194	1.701 303	1.699 528
		1	.432 296	.431 748	.430 655
		2	.306 291	.305 734	.304 626
D_2	0	0	1.805 019	1.804 368	1.803 069
		1	.497 989	.497 604	.496 834
		2	.362 820	.362 400	.361 562
	1	0	1.777 287	1.776 659	1.775 407
		1	.480 505	.480 131	.479 384
		2	.347 694	.347 290	.346 486
	2	0	1.750 205	1.749 603	1.748 404
		1	.463 257	.462 898	.462 180
		2	.332 601	.332 217	.331 450
	3	0	1.723 473	1.722 880	1.721 696
		1	.446 210	.445 849	.445 131
		2	.317 821	.317 445	.316 696

The measured value [54] of the quadrupole coupling constant in the $v = 0, J = 1$ level of the electronic ground state of D_2 is

$$(4.4) \quad eQq = (1.4907 \pm .0015) \times 10^{-21} \text{ ergs}$$

where Q is the deuteron quadrupole moment and

$$(4.5) \quad \begin{aligned} q &= \langle 2R^{-3} \rangle_{0,1} - Q_{zz} \\ Q_{zz} &= \left\langle \sum_{i=1}^2 r_{ai}^{-3} (3 \cos^2 \theta_{ai} - 1) \right\rangle_{0,1} . \end{aligned}$$

Newell [55] calculated $q = .352$ which is close to the value $q = .355$ obtained from the data in Tables 15 and 16. Newell's value of q has been used with (4.4) to obtain the accepted value of Q . Recently, Auffray [56] obtained $q = .339$ with a wave function consisting of 10 of the 40 terms used by KR. He performed a more thorough optimization of the scale factor than KR did and obtained approximately the same electronic energies. It was shown in Section VI 3 that the LCAO-type wave function for H_2^+ gave values of Q_{zz} which were too low. One can infer that a similar deficiency will occur in the MWY wave function and that Auffray's result at least gives a change in the right direction.

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